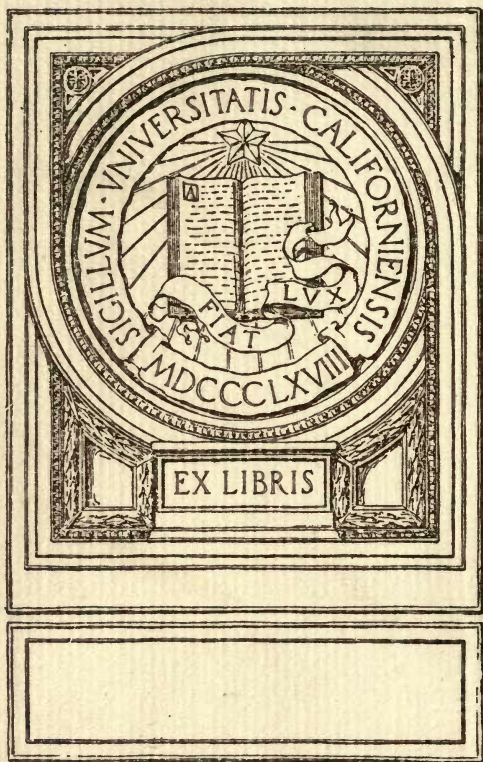


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# THE IDENTIFICATION OF ORGANIC COMPOUNDS.

*Maxon*

By

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## Preface

IN teaching practical organic chemistry we have found the want of a convenient text-book dealing with the identification of simple organic compounds, such as is required by students working for the Intermediate and Final (Branch d) Examinations of the Institute of Chemistry. Moreover, many of the reactions and physical constants are not easily accessible, but are only to be obtained by a diligent and often tedious search through some of the larger books of reference.

In this small volume we have endeavoured to bring together in a convenient form the principal reactions and physical constants of the most important organic substances. Our aim has been to eliminate, as far as possible, guess-work on the part of the student, and to provide him with methods by which he can readily detect the more important groups in the compound, assign it to its class, and then complete its identification by referring to the section dealing with the class to which it belongs. Wherever

possible, an easily prepared derivative is described under each compound.

In many cases descriptions of operations are brief, as we assume that the student has already attended lectures on Organic Chemistry and worked through a satisfactory course of Preparations.

The scheme adopted in this book having given satisfactory results in the laboratories of this College, we now venture to give it wider publicity.

We are deeply indebted to Professor G. G. Henderson for the interest he has taken in the work, and for a number of valuable suggestions.

G. B. N.

I. M. H.

GLASGOW,

*April, 1911.*



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## I. PRELIMINARY TESTS.

1. ORGANIC compounds are often characterized by their appearance and smell, and the experienced student may frequently be able to classify and in some cases to identify a substance by means of these physical properties.

**Colour** is generally induced in a compound by the presence of the following common groups :—

(a) Nitro group. The compound is then generally yellow.

(b) Nitroso group. The compound in the fused state or in solution (if monomolecular) is blue to green in colour.

(c) Azo group and other such related groups. The compound is generally highly coloured.

(d) Compounds having a quinonoid structure are usually strongly coloured. The common quinones are all deep yellow.

2. If the substance is a solid, a small quantity is heated on platinum foil and the changes which occur are carefully noted.

(a) A sooty flame indicates a high percentage of carbon in the substance. The compound is then probably one of the aromatic series.

## 2. THE IDENTIFICATION OF

(b) An incombustible residue indicates the presence of a metal or some inorganic matter in the compound, which is then tested for in the usual manner.

It must be remembered, however, that the metals Mercury and Arsenic, likewise Ammonium salts, are volatile.

3. The solubility of the substance in water is tested.

(a) With the exception of certain salts, substances containing hydroxyl radicles usually dissolve.

(b) The following classes of compounds are also generally soluble :—Lower alcohols, aldehydes, ketones, monobasic acids, polybasic acids, substituted acids, carbohydrates (except starch and cellulose), lower amines and amides, urea and its homologues, thioureas, cyanates, alkyl sulphates.

(c) The solution is tested with litmus.

(i) *An acid reaction* indicates the presence of a carboxyl or sulphonic group in the substance. A salt of a weak base would be hydrolytically dissociated in dilute solution with a resulting acid reaction.

Acid chlorides are rapidly, acid anhydrides slowly, decomposed by water, especially on warming.

(ii) *An alkaline reaction* usually indicates the presence of a free base.

4. A small quantity of the substance (about 0.25 gram) is heated with a large excess of soda-lime in a hard glass test-tube fitted with a cork and a short right-angled delivery tube,



(a) Many nitrogen compounds evolve ammonia. An amine is liberated from an amine salt.

(b) Formates are decomposed with evolution of hydrogen.

(c) Hydrocarbons are produced from carboxy acids or their salts.

(d) Phenols are formed from hydroxy aromatic acids or their salts.

(e) A smell of burnt sugar is observed from carbohydrates, glucosides and many higher acids such as citric acid, tartaric acid, malic acid, tannic acid and gallic acid.

5. The substance is warmed with concentrated caustic soda solution.

(a) Ammonia is evolved from ammonium salts, amides, and imides.

(b) Amines are liberated from their salts. The lower aliphatic amines have characteristic ammoniacal fishy odours and are inflammable. The aromatic amines are insoluble oils or solids.

(c) Acetyl derivatives of amines are decomposed, liberating the free amine. The decomposition is only accomplished by prolonged heating.

(d) Esters are slowly hydrolysed with liberation of the alcohol. The vapours of the lower alcohols are inflammable. The pleasant characteristic odour of the ester disappears.

(e) Acids, phenols and nitrophenols dissolve with formation of a salt. The nitrophenols give red or yellow solutions.

(f) Alkaloids are precipitated from solutions of

their salts. Morphine is only slowly precipitated from a solution of its salt and is readily soluble in excess of the reagent.

(g) Aliphatic aldehydes, with the exception of formaldehyde, are converted into resins.

(h) Solutions of glucose and lactose are turned brown.

6. Dilute sodium carbonate solution is added to a small quantity of the substance contained in a test-tube, and the mixture is gently warmed. Acids, chlorophenols, nitrophenols and polyhydric phenols readily dissolve. Monohydric phenols are insoluble.

7. In order to ascertain if the substance is a saturated or unsaturated compound, a small quantity is dissolved in chloroform or in some suitable solvent having no action on bromine and a dilute solution of bromine in the same solvent is added, drop by drop. If the bromine is instantly decolourized without a simultaneous evolution of hydrobromic acid, the presence of a double or treble bond is shown, the substance being unsaturated.

## II. TESTS FOR THE ELEMENTS.

Oxygen cannot be detected by any direct test, and the indications of its presence in a substance must be inferred from the foregoing experiments.

It is not generally necessary to make any special tests for **Carbon** and **Hydrogen**.

The presence of **Nitrogen** in an organic substance is indicated by heating a small quantity of the compound in a hard glass test-tube with excess of soda-lime. If ammonia is evolved, the presence of nitrogen is proved.

As, however, nitro-compounds, azo-compounds and some other nitrogen compounds do not respond to this test, the following delicate test must be applied before the absence of nitrogen may be considered conclusively proved.

A small piece of sodium, about the size of a pea, is dropped into a dry hard glass test-tube and gently warmed till it melts, after which a little of the substance, about 0.1 gram, is introduced in such a manner that it falls directly on the sodium. If the substance is a liquid it is allowed to fall drop by drop on the sodium, care being taken to prevent it touching the sides of the tube. After the first violent action has ceased, the tube is heated in a Bunsen flame till all apparent change is over.

The tube is allowed to cool and 10 cc. water are carefully added. The mixture is boiled for a few minutes and, if necessary, filtered from any carbonaceous matter.

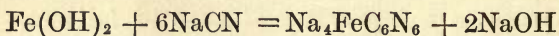
If the filtrate be divided into three portions the presence of a **halogen** or of **sulphur** in the substance may also be directly tested.

One portion of the original solution or filtrate is now treated with a few drops of caustic soda solu-

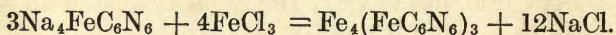
tion, a little freshly-prepared ferrous sulphate solution and finally a few drops of ferric chloride solution, and the whole well shaken. On carefully acidifying with concentrated hydrochloric acid a blue solution or precipitate of Prussian blue is formed, proving the presence of nitrogen in the original substance.

*Note.*—With substances containing only a small percentage of nitrogen a greenish-blue solution is frequently obtained which may only show the Prussian blue precipitate after standing for a considerable time.

The formation of the Prussian blue depends on the fact that the nitrogen and carbon combine with the sodium to yield sodium cyanide. This compound in presence of ferrous hydroxide combines to give sodium ferrocyanide—



After the addition of ferric chloride and acid the insoluble Prussian blue is precipitated—



After testing the one portion for the presence of nitrogen another portion is acidified with nitric acid, the solution boiled to expel any hydrocyanic acid present, and then silver nitrate solution is added. If a precipitate is formed the presence of a halogen in the original substance is indicated and its nature may be determined by submitting the precipitate to the usual examination for the detection of chlorine, bromine, or iodine. This test depends on the



formation of sodium halide produced by combination of any halogen in the original substance with the metallic sodium.

Another simple test to prove the presence of a halogen in a substance is obtained by wrapping a small piece of copper oxide within a stout copper wire, heating it in a Bunsen flame until no green colouration is produced, and allowing it to cool. A very small quantity of the substance is then placed on the oxide, which is again heated in the flame, when, if a halogen be present, a green colouration is observed, due to the formation of a volatile halogen compound of copper. This test is not absolutely conclusive, as some non-halogen-compounds appear able to produce a similar colouration. Further, by this test, no information is obtained as to which halogen is present.

**Sulphur** in a compound is best detected by taking the third portion from the sodium extract as already described, and placing a drop of the alkaline solution on a silver coin. If the original substance contained sulphur, sodium sulphide will have been produced, forming on the silver coin a black precipitate of silver sulphide.

The presence of sodium sulphide in the alkaline filtrate is also readily detected by the addition of sodium nitroprusside solution, which produces a deep violet colouration with an alkali sulphide.

**Phosphorus** may be detected by fusing a small quantity of the substance with a mixture of equal portions of potassium nitrate and carbonate on a

piece of platinum foil. The residue is dissolved in water, acidified with a few drops of concentrated nitric acid and a phosphate tested for in the usual way with ammonium molybdate.

### III. GROUP REACTIONS.

FROM the foregoing preliminary tests the student will have deduced the type of compound with which he is dealing, or at any rate something of its nature. The following tests for individual groups may now be performed :—

#### HYDROXYL GROUP.

(a) A small quantity of the compound is heated for about fifteen minutes with an excess of acetic anhydride.

If a hydroxyl group is present an acetyl derivative (oily or crystalline) is thus formed which may then be separated, washed with dilute sodium carbonate solution and finally hydrolysed by heating under a reflux condenser with caustic soda solution. The acetyl compound is, in this way, decomposed with formation of an acetate which can readily be recognized by applying the usual tests for acetic acid or acetates (*see* page 38).

(b) SCHOTTEN-BAUMANN REACTION.—About 1

gram of the compound is vigorously shaken up with about 1 cc. benzoyl chloride and sufficient dilute caustic soda solution to render the mixture alkaline. The product is poured into water and the crystalline benzoate separated by filtration, washed with water and then hydrolysed with caustic soda solution. After hydrolysis an alkali benzoate is formed, which can be detected in the usual manner (see page 41).

If required, the benzoyl derivative may be purified by recrystallization from alcohol, and its melting point determined.

### METHOXY AND ETHOXY GROUPS.

Seven cc. hydriodic acid (Sp. Gr. 1.7) are added to about 0.2 gram of the compound in a test-tube fitted with cork and delivery tube, the end of which dips into an alcoholic solution of silver nitrate. The mixture is very gently heated in a glycerine bath to  $140^{\circ}$  and, if a methoxy or ethoxy group be present, methyl or ethyl iodide distils over and produces a precipitate of silver iodide in the alcoholic silver nitrate solution.

### ALDEHYDE GROUP.

(a) TOLLEN'S REACTION.—Ammonium hydroxide solution is cautiously added to about 2 cc. silver nitrate solution until the precipitate which is first formed is just redissolved. One cc. caustic soda solution is next run in and then 2 or 3 drops of

the supposed aldehyde solution. If an aldehyde group is present an immediate deposit of metallic silver is produced in the cold.

(b) SCHIFF'S REACTION.—A few drops of the aldehyde are poured into about 5 cc. of a solution of Schiff's reagent (magenta solution which has been decolourized by sulphur dioxide). The red colouration of the magenta is immediately restored.

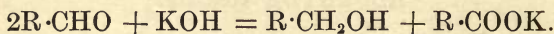
It should be noted that some ketones if present in large quantity react similarly, although the reappearance of the colour is more gradual and shows first after the mixture has stood for some time.

(c) Fehling's solution is rapidly decomposed with precipitation of red cuprous oxide on being warmed with an aliphatic aldehyde.

Aromatic aldehydes do not give this reaction.

(d) If about 1 cc. of an aliphatic aldehyde is warmed with 2 cc. concentrated caustic potash solution, a brown precipitate of aldehyde resin separates out.

Formaldehyde and aromatic aldehydes do not react in this manner, but yield mixtures of alcohols and acids, both containing the same number of carbon atoms as the original aldehyde.



(e) If 1 cc. of an aldehyde is vigorously shaken up in a test-tube with a few cc. of a cold saturated solution of sodium hydrogen sulphite<sup>1</sup> a precipitate

<sup>1</sup> See Appendix, page 100.



of the aldehyde "bisulphite compound" is formed. Sodium carbonate solution liberates the aldehyde from the acid sulphite compound.

Some ketones produce similar crystalline compounds.

### KETONE GROUP.

If an aldehyde group is absent the presence of a ketone group may be confirmed by the preparation of the semicarbazone of the ketone (*see* page 30 for this preparation).

### AMINO GROUP.

(a) CARBYLAMINE TEST : —About 0.1 gram of the substance is mixed with 3 drops of chloroform and 2 cc. alcoholic potash, and the whole carefully warmed. The characteristic disgusting carbylamine odour is produced if the substance contains an amino group.

(b) A small quantity of the compound is dissolved in a few cc. hydrochloric acid and sodium nitrite solution is then added until an excess of free nitrous acid is present. On warming, the amino group is converted into hydroxyl, with a vigorous evolution of nitrogen.

Aliphatic amines and aromatic amines having the amino group in a side chain produce alcohols.

Aromatic primary amines with the amino group in the nucleus form phenols.

To distinguish between the two classes of aromatic amines, the amine is diazotized (*see* page 64) in the cold, and a solution of  $\beta$ -naphthol in caustic soda added. An intensely coloured azo dye is produced if the amino group is in the nucleus.

### IMINO GROUP.

If sodium nitrite is added to an acid solution of the compound, a yellow precipitate or solution of a nitrosoamine is formed, which may be confirmed by applying LIEBERMANN'S TEST for nitrosoamines :—

The precipitate or solution containing the nitrosoamine is extracted with ether, the ethereal solution washed and dried rapidly over calcium chloride and the ether then blown off. To the residue, oil or solid, is now added a small quantity of phenol and 4 to 5 drops concentrated sulphuric acid, when a deep greenish black colouration is produced. On pouring the mixture into water a red solution is formed, which is changed to blue or green on addition of alkalies.

*Note.*—With aliphatic tertiary amines no reaction results on addition of nitrous acid, but dialkylanilines interact readily, intensely coloured green nitroso compounds being formed, the NO-group displacing hydrogen of the benzene nucleus from the para position to the nitrogen atom. Substances of this type do not give Liebermann's reaction.

The hydrochlorides of these para-nitroso bodies,

which would be precipitated on addition of sodium nitrite to a hydrochloric acid solution of a dialkylamine, are generally yellow in colour and must not be confounded with the secondary nitrosoamines.

### NITRO GROUP.

A small quantity of the substance is mixed in a test-tube with about 2 cc. concentrated hydrochloric acid and to this 1 gram zinc dust is gradually added in small quantities, and the mixture finally warmed. About 5 cc. water are now run in and then concentrated caustic alkali until the precipitate at first formed is redissolved. The amine produced is extracted with ether, and the presence of the amino group can be recognized by the tests given in the preceding paragraph.

### NITRILES AND ISONITRILES.

(a) A small quantity of the substance is heated with 20 cc. concentrated hydrochloric acid under a reflux condenser. The reaction mixture is then made alkaline with caustic soda and heated.

Ammonia is evolved from nitriles, whereas the isonitriles yield under the same conditions sodium formate and an amine.

(b) MENDIUS' REACTION FOR NITRILES.<sup>1</sup>—Nitriles, when reduced in a similar manner to that described for the reduction of nitro-compounds, yield amines which can readily be isolated and identified.

<sup>1</sup> See page 74.

**AZO-GROUP.**

Azo dye-stuffs when vigorously reduced, yield amines, either simple or complex. About 1 gram of the substance is treated with about 20 cc. of a concentrated solution of stannous chloride in hydrochloric acid. Caustic soda solution is then added until the precipitate first formed is just redissolved. Free amines are liberated which may be separated, and the usual tests for the amino group applied.

**IV. HYDROCARBONS.**

THESE are generally colourless liquids or solids, practically insoluble in water, soluble in alcohol and ether. The solubility in the last mentioned solvents decreases with increase in the molecular weight of the compound.

**ALIPHATIC HYDROCARBONS.**

*n*-Pentane,  $C_5H_{12}$ , is an exceptionally stable colourless liquid, boiling at  $36-37^\circ$ .

*n*-Hexane,  $C_6H_{14}$ , boils at  $69-70^\circ$ .

*n*-Heptane,  $C_7H_{16}$ , boils at  $97-98^\circ$ .

*n*-Octane,  $C_8H_{18}$ , boils at  $124^\circ$ .

Isoprene,  $\begin{smallmatrix} CH_2 \\ CH_3 \end{smallmatrix} > C \cdot CH = CH_2$ , is a colourless liquid

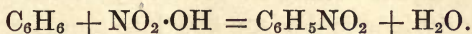


boiling at  $37^{\circ}$ , obtained by dry distillation of caoutchouc. Concentrated hydrochloric acid converts isoprene into a substance very similar to, if not identical with, caoutchouc.

### AROMATIC HYDROCARBONS.

**Benzene**,  $C_6H_6$ , B.P.  $80-81^{\circ}$ , M.P.  $5.4^{\circ}$ . The pure hydrocarbon has a peculiar, not unpleasant smell. It is exceedingly stable towards oxidizing agents.

If 1 gram of the hydrocarbon be added to a mixture of 3 grams concentrated sulphuric acid and 2 grams concentrated nitric acid (Sp. Gr. 1.4), and the mixture warmed on a water-bath for about  $\frac{1}{2}$  hour at  $60^{\circ}$ , nitro-benzene is obtained, and on cooling may be separated from the lower layer of acids, washed, dried and identified [(see page 70)



**Toluene**,  $C_6H_5 \cdot CH_3$ , B.P.  $110^{\circ}$ . Toluene on treatment with chromic acid yields benzoic acid.

About 1 gram of the substance is heated under a reflux condenser with a mixture consisting of 2 parts potassium dichromate, 3 parts concentrated sulphuric acid and 3 of water. After oxidation the solution is filtered while hot, when on cooling benzoic acid separates out and may be tested for as shown on page 41.

**o-Xylene**,  $C_6H_4 \begin{smallmatrix} \swarrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$  boils at  $142^{\circ}$ . With dilute potassium permanganate it yields phthalic acid.

A small quantity of the hydrocarbon is heated under a reflux condenser for some time with dilute alkaline potassium permanganate. The solution is then, if necessary, treated with sulphurous acid to remove excess of potassium permanganate, filtered off from the separated manganese dioxide and acidified. The acid is then extracted with ether, dried with calcium chloride and the tests for phthalic acid applied (*see* page 42).

*m*-Xylene and *p*-Xylene, boiling points  $139^{\circ}$  and  $138^{\circ}$  respectively, are distinguished from each other by the fact that the meta-compound is sulphonated in the cold with sulphuric acid, while the para-compound remains unchanged.

Ethylbenzene,  $C_6H_5 \cdot C_2H_5$ , boils at  $134^{\circ}$ . Chromic acid oxidizes it to benzoic acid.

Mesitylene,  $C_6H_3(CH_3)_3$  1 : 3 : 5, is an agreeably smelling liquid boiling at  $163-164^{\circ}$ . With chromic acid mesitylene is decomposed into acetic acid.

Cumene,  $C_6H_5 \cdot CH(CH_3)_2$ , is a colourless liquid boiling at  $152-153^{\circ}$ . On oxidation with chromic acid or dilute nitric acid it is converted into benzoic acid.

Cymene,  $C_6H_4 \begin{matrix} \swarrow CH_3 \\ \searrow CH(CH_3)_2 \end{matrix} \begin{matrix} (1) \\ (4) \end{matrix}$ , is a pleasant smelling liquid boiling at  $175^{\circ}$ .

Diphenyl,  $C_6H_5 \cdot C_6H_5$ , is a colourless, crystalline solid, melting at  $71^{\circ}$ , B.P.  $254^{\circ}$ ; when oxidized with chromic acid it is converted into benzoic acid.

Diphenylmethane,  $C_6H_5 \cdot CH_2 \cdot C_6H_5$ , is a crystalline solid, M.P.  $26.5^{\circ}$ . On oxidation with chromic acid

it is converted into benzophenone which may be extracted with ether and identified (page 37).

**Stilbene**,  $C_6H_5 \cdot CH : CH \cdot C_6H_5$ , crystallizes in colourless needles, M.P.  $124-125^\circ$ . It is unsaturated and readily adds on two atoms of bromine forming stilbene dibromide,  $C_6H_5 \cdot CHBr \cdot CHBr \cdot C_6H_5$ , M.P.  $137^\circ$ . Oxidation with chromic acid or alkaline permanganate yields benzoic acid.

**Styrene**,  $C_6H_5 \cdot CH : CH_2$ , is a colourless liquid which boils at  $145^\circ$ . It is oxidized to benzoic acid with chromic acid mixture.

**Phenylacetylene**,  $C_6H_5 \cdot C : CH$ , is a colourless liquid boiling at  $139-140^\circ$ . It yields a yellow copper compound when mixed with ammoniacal cuprous chloride solution. On oxidation with chromic acid, benzoic acid is obtained.

**Naphthalene**,  $C_{10}H_8$ , crystallizes in lustrous leaflets which melt at  $80^\circ$  and boil at  $218^\circ$ . It has a characteristic smell, and is very volatile. On addition of a solution of the hydrocarbon in benzene to a solution of picric acid in the same solvent, a yellow crystalline compound, naphthalene picrate,  $C_{10}H_8, C_6H_2(NO_2)_3OH$  melting at  $149^\circ$  separates out on standing. Naphthalene on boiling with dilute nitric acid is oxidized, yielding phthalic acid and carbon dioxide.

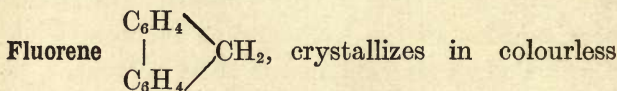
**Anthracene**,  $C_{14}H_{10}$ , crystallizes in almost colourless lustrous plates, possessing a beautiful violet fluorescence. It melts at  $213^\circ$ , boils at  $360^\circ$ . With picric acid it forms the molecular compound  $C_{14}H_{10}, C_6H_2(NO_2)_3OH$  which is deposited from

benzene solution in ruby-red needles melting at  $138^{\circ}$ .

Anthracene is readily oxidized to anthraquinone by dissolving the hydrocarbon in warm glacial acetic acid and adding to the solution about double the weight of chromic anhydride, and then boiling for a short time. The mixture is largely diluted with water, the anthraquinone filtered off, washed with dilute sulphuric acid, then with water and finally dried. M.P.  $273^{\circ}$ .

Phenanthrene,  $C_{14}H_{10}$ , forms colourless leaflets melting at  $99^{\circ}$ . It is readily soluble in alcohol, while the isomeric anthracene is only sparingly soluble.

It combines with picric acid to give a yellow compound, phenanthrene picrate, melting at  $144^{\circ}$ . With chromic anhydride it yields phenanthraquinone, M.P.  $205^{\circ}$ .



leaflets with a violet fluorescence. It melts at  $113^{\circ}$ . The picrate obtained by mixing benzene solutions of fluorene and picric acid melts at  $79-80^{\circ}$ .



## V. ALCOHOLS.

THE common monohydric alcohols are, as a rule, colourless liquids (diphenyl and triphenyl carbinols are solids) with a neutral reaction and possessing a characteristic smell and taste. The lower members are soluble in water, but the solubility rapidly decreases with increase of molecular weight. The Sp. Gr. is always less than that of water.

The polyhydric alcohols are oily liquids or crystalline solids, all readily soluble in water, sparingly soluble or insoluble in ether.

### PRIMARY MONOHYDRIC ALCOHOLS.

Methyl alcohol,  $\text{CH}_3\text{OH}$ , is a colourless, mobile liquid boiling at  $66.5^\circ$ . It burns with a bluish non-luminous flame. If a mixture of methyl alcohol with dilute sulphuric acid and potassium dichromate be distilled, the distillate contains formic acid which may be identified (page 38).

When methyl alcohol is heated with salicylic acid and concentrated sulphuric acid, methyl salicylate is formed and can be identified by its odour. On warming methyl alcohol with paranitrobenzoyl chloride, the methyl ester is formed, melting at  $96^\circ$ .

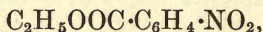
Ethyl Alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , boils at  $78^\circ$ .

1. When ethyl alcohol is mixed with a little dilute sulphuric acid and potassium dichromate and the mixture warmed, the alcohol is oxidized to acetalde-

hyde which can be recognized by its peculiar choking smell.

2. The formation of Iodoform serves as a delicate test for ethyl alcohol.<sup>1</sup> To a solution of alcohol a little sodium carbonate is added and the mixture warmed to about 60°. To this is now added drop by drop, a strong solution of iodine in potassium iodide until, after shaking, the liquid remains faintly brown. Iodoform separates out, having a characteristic odour and melting at 119°.

3. The para-nitrobenzoic-ester,



is readily obtained as a crystalline solid melting at 57°.

Propyl alcohol,  $\text{C}_3\text{H}_7\text{OH}$ , boils at 97.4°. It is miscible in all proportions with water, but on addition of calcium chloride and other easily soluble salts it separates out from its aqueous solution.

Normal Butyl Alcohol,  $\text{C}_4\text{H}_9\text{OH}$ , is a liquid with an agreeable odour boiling at 117°.

Isobutyl Alcohol,  $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH} \cdot \text{CH}_2\text{OH}$ , is a liquid possessing a fusel-oil odour. B.P. 108°.

Normal Amyl Alcohol,  $\text{C}_5\text{H}_{11}\text{OH}$ , is a liquid almost insoluble in water, boiling at 137°.

Allyl Alcohol,  $\text{C}_3\text{H}_5\text{OH}$  ( $\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{OH}$ ), is a mobile liquid with a pungent odour, boiling at 96.5°. It has the properties not only of a primary alcohol, but also of an unsaturated compound.

<sup>1</sup> Acetone also gives the Iodoform test.

On distilling allyl alcohol with chromic acid, formic acid (page 38) distils over.

**Benzyl Alcohol**,  $C_6H_5 \cdot CH_2OH$ , is a colourless liquid, with a faint aromatic odour and boils at  $206^\circ$ . It is sparingly soluble in water, readily in alcohol and ether. On oxidation with dilute nitric acid it yields first benzaldehyde and then benzoic acid.

### SECONDARY MONOHYDRIC ALCOHOLS.

**Isopropyl Alcohol** ( $CH_3 \cdot CHOH \cdot CH_3$ ), boils at  $82-83^\circ$ . Oxidizing agents convert it into acetone.

**Diphenyl Carbinol**, benzhydrol,  $(C_6H_5)_2CHOH$ , crystallizes in silky needles, very sparingly soluble in water, M.P.  $67-68^\circ$ . The acetate melts at  $41-42^\circ$ .

### TERTIARY MONOHYDRIC ALCOHOLS.

**Tertiary Butyl Alcohol**,  $(CH_3)_3COH$ , is a colourless solid melting at  $25^\circ$ , boiling at  $83-84^\circ$ .

**Triphenyl Carbinol**,  $(C_6H_5)_3COH$ , M.P.  $159^\circ$ . The acetate melts at  $99^\circ$ .

### POLYHYDRIC ALCOHOLS.

**Ethylene Glycol**,  $CH_2OH \cdot CH_2OH$ , is a thick colourless liquid boiling at  $197-198^\circ$ . When glycol is heated with solid caustic potash to  $250^\circ$ , hydrogen is evolved and potassium oxalate formed which may be identified (*see* page 39).

**Glycerol**,  $C_3H_5(OH)_3$ , is a colourless, syrupy liquid with a sweet taste, insoluble in ether.

When glycerol is heated with potassium hydrogen

sulphate, or with phosphoric anhydride, acrolëin is produced and may be identified by its pungent disagreeable odour.

When a borax bead is moistened with glycerol and held near the outer edge of a Bunsen flame it gives a green colouration.

The following are crystalline solids :—

**Erythritol**,  $C_4H_6(OH)_4$ , M.P.  $112^\circ$ .

Oxidation with conc. nitric acid converts erythritol into oxalic acid. The tetra-benzoate melts at  $186-187^\circ$ .

**Arabitol**,  $CH_2OH(CHOH)_3CH_2OH$ , M.P.  $102^\circ$ .

**Mannitol**,  $CH_2OH(CHOH)_4CH_2OH$ , M.P.  $166^\circ$ .

The hexabenzoate melts at  $124-125^\circ$ , the hexacetate at  $119^\circ$ .

## VI. ETHERS.

THESE are neutral, volatile liquids, practically insoluble in water and chemically very indifferent. They can be best identified by their boiling points.

**Ethyl Ether**,  $(C_2H_5)_2O$ , B.P.  $34-35^\circ$ .

**Normal Propyl Ether**,  $(C_3H_7)_2O$ , B.P.  $90-91^\circ$ .

**Anisol**,  $C_6H_5 \cdot O \cdot CH_3$  is an ethereal smelling liquid boiling at  $154-155^\circ$ . Heated with concentrated hydriodic acid to  $140^\circ$  it decomposes into phenol and methyl iodide.

**Phenetol**,  $C_6H_5 \cdot O \cdot C_2H_5$ , boils at  $172^\circ$ .



**Phenyl Ether**,  $\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{C}_6\text{H}_5$ , crystallizes in long needles and possesses a smell resembling geraniums. It melts at  $28^\circ$ , boils at  $252^\circ$ . It is not reduced on heating with hydriodic acid.

## VII. PHENOLS.

THE phenols, with the exception of *m*-cresol are crystalline solids. They are of an acid nature, the hydrogen of the hydroxyl being readily substituted by metals. The monohydric phenols are but sparingly soluble in water, the polyhydric phenols readily soluble.

**Phenol**,  $\text{C}_6\text{H}_5\text{OH}$ , is a colourless crystalline solid, which gradually acquires a reddish colour, and deliquesces on exposure to air. It melts at  $43^\circ$ , boils at  $181^\circ$ ; it dissolves in 15 parts water and gives a violet colouration in neutral solution with ferric chloride.

When an aqueous solution of phenol is mixed with one-fourth of its volume of ammonia solution and then with a few drops of a bleaching powder solution, and gently warmed, a fine blue colour is produced, which soon disappears.

Bromine water precipitates tribromophenol from solutions as an oil which soon crystallizes and melts at  $92^\circ$ . The crude tribromophenol may if necessary be purified by recrystallizing from alcohol. The benzoate melts at  $69^\circ$ .

*o*-Cresol,  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_3 \\ \text{OH} \end{matrix}$  M.P.  $31^\circ$ . On fusion

with potassium hydroxide, salicylic acid is formed. With picric acid, a picrate,  $2\text{C}_7\text{H}_5\text{O}, 3\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , melting at  $88^\circ$  is obtained in orange yellow needles.

*m*-Cresol is liquid and boils at  $202\text{--}203^\circ$ . Ferric chloride colours an aqueous solution of *m*-cresol deep blue violet. The benzoate melts at  $54^\circ$ .

*p*-Cresol melts at  $36^\circ$  and gives with ferric chloride a blue colouration. The benzoate melts at  $71\text{--}72^\circ$ .

Carvacrol,  $\begin{matrix} \text{CH}_3 \\ \text{C}_6\text{H}_4 \\ \text{C}_3\text{H}_7 \end{matrix}$  OH is a thick oil boiling at  $236\text{--}237^\circ$ . An alcoholic solution of carvacrol is coloured green on addition of ferric chloride.

Thymol,  $\begin{matrix} \text{CH}_3 \\ \text{C}_6\text{H}_4 \\ \text{C}_3\text{H}_7 \end{matrix}$  OH melts at  $50\text{--}51^\circ$ , and possesses

a pleasant aromatic odour. An aqueous solution of thymol treated with one half its volume of glacial acetic acid and one volume of concentrated sulphuric acid produces on warming a red violet colouration.

$\alpha$ -Naphthol,  $\text{C}_{10}\text{H}_7\text{OH}$ , melts at  $94^\circ$ , is practically insoluble in cold water, readily soluble in alcohol and ether. Bleaching powder solution produces a dark violet colouration. A naphthol picrate is

produced, by mixing alcoholic solutions of the components, in orange needles melting at  $189^{\circ}$ .

*a*-Naphthol acetate melts at  $46^{\circ}$ .

PREPARATION OF ACETATE.—One gram of the naphthol is boiled for about fifteen minutes with 2 grams acetic anhydride. On pouring the product into water the crude acetate separates out. It is purified by recrystallization from a small quantity of water.

*a*-Naphthol benzoate melts at  $56^{\circ}$ .

*β*-Naphthol melts at  $122^{\circ}$ . With ferric chloride a greenish colouration is produced in an aqueous solution of the naphthol, from which after some time a white flocculent precipitate is thrown down. *β*-Naphthol dissolved in strong potassium hydroxide solution and treated with chloroform produces on warming to  $50^{\circ}$  a blue colouration which gradually becomes green and finally brown. *β*-Naphthol acetate,  $C_{10}H_7OOC \cdot CH_3$ , melts at  $70^{\circ}$ . The benzoate melts at  $107^{\circ}$ .

Catechol (pyrocatechin),  $C_6H_4 \begin{smallmatrix} \text{OH}(1) \\ \text{OH}(2) \end{smallmatrix}$ , melts at  $104^{\circ}$ . It reduces Fehling's solution on warming. With lead acetate a white precipitate is obtained. Ferric chloride produces in an aqueous solution of catechol an emerald-green colouration, which on addition of sodium bicarbonate becomes violet-red.

Guaiacol,  $C_6H_4 \begin{smallmatrix} \text{OCH}_3(1) \\ \text{OH}(2) \end{smallmatrix}$ , melts at  $31^{\circ}$ . Ferric chloride gives its alcoholic solution an emerald-green colour.

**Resorcinol**,  $C_6H_4 \begin{smallmatrix} \text{OH (1)} \\ \text{OH (3)} \end{smallmatrix}$ , M.P.  $118^\circ$ . Ferric chloride produces a dark violet colouration. If equal weights of resorcinol and phthalic anhydride are gently heated together in a test-tube a yellow melt is obtained, which, when dissolved in dilute caustic soda solution, produces a solution showing a fine green fluorescence (formation of fluorescein). Bromine water precipitates tribromoresorcinol, M.P.  $111^\circ$ , from an aqueous solution of resorcinol. The dibenzoate melts at  $117^\circ$ .

**Quinol (hydroquinone)**,  $C_6H_4 \begin{smallmatrix} \text{OH (1)} \\ \text{OH (4)} \end{smallmatrix}$ , melts at  $169^\circ$  and is readily soluble in water, alcohol and ether.

With ferric chloride quinhydrone is readily obtained in beautiful metallic green crystals by adding ferric chloride to a concentrated solution of hydroquinone in water. The solution becomes at first red and then rapidly darkens.

The diacetate and the dibenzoate melt respectively at  $123^\circ$  and  $199^\circ$ .

**Orcinol**,  $C_6H_3 \begin{smallmatrix} \text{CH}_3 \text{ (1)} \\ \text{OH (3)} \\ \text{OH (5)} \end{smallmatrix}$ , M.P.  $107^\circ$ , is easily soluble

in water, alcohol and ether. On exposure to the air it becomes red. With ferric chloride a violet-black colouration is produced. Bleaching powder solution produces a dark red colouration which soon changes to yellow. The diacetate melts at  $25^\circ$ , the dibenzoate at  $88^\circ$ .

**Pyrogallol**,  $C_6H_3(OH)_3$  1 : 2 : 3, melts at  $132\text{--}133^\circ$



and is readily soluble in water, alcohol and ether. An alkaline solution of pyrogallol quickly absorbs oxygen from the air and becomes brown. An aqueous solution of pyrogallol is turned brown on addition of nitrous acid solution. The tribenzoate melts at  $90^{\circ}$ .

Phloroglucinol,  $C_6H_3(OH)_3$  1 : 3 : 5, melts at  $218^{\circ}$  on quickly heating. It is readily soluble in water, alcohol and ether. With ferric chloride a blue-violet colouration is obtained. The acetate melts at  $105^{\circ}$ , the benzoate at  $173^{\circ}$ . The trioxime melts at  $43^{\circ}$ .

### ALCOHOL PHENOLS.

Saligenin,  $C_6H_4 \begin{matrix} \text{OH} \\ \text{CH}_2\text{OH} \end{matrix} \begin{matrix} (1) \\ (2) \end{matrix}$ , M.P.  $86^{\circ}$ , is very readily soluble in boiling water, alcohol and ether. It dissolves in concentrated sulphuric acid with an intense red colour. With ferric chloride it gives a blue colouration.

Anisyl Alcohol,  $C_6H_4 \begin{matrix} \text{OCH}_3 \\ \text{CH}_2\text{OH} \end{matrix} \begin{matrix} (1) \\ (4) \end{matrix}$ , melts at  $45^{\circ}$ .

Dilute nitric acid oxidizes it to anisic acid, M.P.  $185^{\circ}$ .

### HALOGEN PHENOLS.

*o*-Chlorophenol,  $C_6H_4 \begin{matrix} \text{OH} \\ \text{Cl} \end{matrix}$ , has an unpleasant odour and boils at  $175\text{--}176^{\circ}$ .

*m*-Chlorophenol is obtained as crystals melting at  $28.5^{\circ}$ .

*p*-Chlorophenol melts at 37°. It possesses a faint, unpleasant odour. Fused with alkalis it gives resorcinol.

*o*-Bromophenol is an unpleasant-smelling oil, boiling at 194–195°.

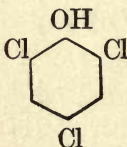
*m*-Bromophenol melts at 32–33°.

*p*-Bromophenol melts at 63–64°.

*o*-Iodophenol is obtained as needles, melting at 43°. It is fairly soluble in hot water, readily soluble in alcohol and ether. By warming with nitric acid (Sp. Gr = 1.2) picric acid is formed.

*m*-Iodophenol melts at 40°.

*p*-Iodophenol forms long needles melting at 92°. By boiling with nitric acid it is readily converted into picric acid.

Trichlorophenol,  melts at 67–68° and

has an acid reaction. With hydrochloric acid and potassium chlorate, chloranil (*see* page 59) is formed.

Tribromophenol (2 : 4 : 6) melts at 95°. The acetate recrystallized from alcohol melts at 82°.

### AMINOPHENOLS

*o*-Aminophenol,  $C_6H_4 \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$ , when pure is colourless, but readily becomes brown. It melts at 170°, and is somewhat sparingly soluble in water, readily in ether. The acetate melts at 150°.

*p*-Aminophenol melts with decomposition at 184°. With chromic acid it is readily oxidized to quinone.

*p*-Aminophenol Methyl Ester (*pp*—. anisidine)

$\text{C}_6\text{H}_4 \begin{matrix} \text{OCH}_3 & (1) \\ \text{NH}_2 & (4) \end{matrix}$  forms plates melting at 52–56°.

Phenacetin,  $\text{C}_6\text{H}_4 \begin{matrix} \text{OC}_2\text{H}_5 & (1) \\ \text{NHCOCH}_3 & (4) \end{matrix}$  melts at 135°.

On hydrolysis with caustic soda it yields sodium acetate, and phenetidine, B.P. 244°.

## VIII. ALDEHYDES.

THE lower aldehydes are volatile liquids soluble in water and possessing a characteristic odour. The higher members of the series are solids, insoluble in water.

In chemical properties the aldehydes are neutral substances, easily oxidized to corresponding acids, their ready oxidation by the salts of the noble metals being one of the characteristics of the aldehydes.

All aldehydes form oximes with hydroxylamine, phenylhydrazones with phenylhydrazine and semicarbazones with semicarbazide hydrochloride. As these derivatives can readily be obtained in the pure state and are generally solids, their preparation and melting-point determination serve as an aid in the identification of an aldehyde.

PREPARATION OF AN OXIME.—One gram of the

aldehyde dissolved in the least possible quantity of alcohol is treated with a slight excess of hydroxylamine hydrochloride dissolved in a little water. To this mixture is added the theoretical quantity of sodium hydroxide in concentrated solution. If any precipitate is now formed, alcohol or water, as may be necessary, is added to bring about complete solution. The solution is then heated on a water-bath under a reflux condenser for from one to two hours. The reaction mixture is then poured into water, made faintly acid with acetic acid and the oxime extracted with ether, the ethereal solution dried, the ether distilled off and the oxime recrystallized from some suitable solvent.

**PREPARATION OF A PHENYLHYDRAZONE.**—One cc. phenylhydrazine is added to about 5 cc. water and sufficient acetic acid added, with vigorous shaking, to bring about complete solution. About 0.5 gram of the aldehyde is now added (in solution if necessary) and the mixture vigorously shaken and very gently warmed. The phenylhydrazone separates out and, if solid, is filtered off, washed with dilute acetic acid, dried on a porous plate or between filter paper, and finally recrystallized from alcohol or benzene.

**PREPARATION OF A SEMICARBAZONE.**—One gram of the aldehyde, dissolved in the smallest possible quantity of alcohol is added to a solution containing 2 grams semicarbazide hydrochloride dissolved in the minimum quantity of water. A cold alcoholic solution containing 2 grams potassium acetate, best



prepared by boiling the acetate with alcohol, is now added, and, if any precipitate forms, water or alcohol, as the case requires, is then carefully added until a clear solution is obtained. The mixture is then allowed to stand for some hours, the aldehyde semicarbazone gradually separating out.

The addition of a few drops of methyl alcohol (free from acetone) often accelerates the separation of the semicarbazone. The semicarbazone obtained is finally recrystallized from methyl or ethyl alcohol.

**Formaldehyde**,  $\text{H}\cdot\text{CHO}$ , is gaseous at the ordinary temperature and is usually met with in solution, the aqueous solution possessing a penetrating, suffocating odour. When its aqueous solution is mixed with ammoniacal silver nitrate solution a silver mirror is obtained.

**Trioxymethylene**  $(\text{H}\cdot\text{CHO})_3$ , is a crystalline compound which sublimes readily under  $100^\circ$ . When strongly heated it is decomposed into pure gaseous formaldehyde. It is readily soluble in cold sodium hydroxide solution, insoluble in alcohol and ether.

**Acetaldehyde**,  $\text{CH}_3\cdot\text{CHO}$ , is obtained as a strongly-smelling suffocating liquid, boiling at  $21^\circ$  and miscible in all proportions with water. Boiling with potassium hydroxide solution produces the yellow-brown aldehyde resin. Acetaldehyde combines readily with ammonia gas to give aldehyde ammonia, a colourless crystalline solid. Its phenylhydrazone melts at  $99^\circ$ , the semicarbazone at  $162^\circ$ , the oxime at  $47^\circ$ .

**Para-aldehyde**  $(\text{C}_2\text{H}_4\text{O})_3$ , boils at  $124^\circ$  and on dis-

tillation is completely converted into acetaldehyde. It gives none of the usual aldehyde reactions.

**Meta-aldehyde**  $(C_2H_4O)_3$ , is isomeric with para-aldehyde. It is a crystalline solid which sublimes at  $112^\circ$  without melting. On distillation with dilute sulphuric acid it breaks down into acetaldehyde. Like para-aldehyde it gives none of the aldehyde reactions.

**Aldol**,  $CH_3 \cdot CH(OH)CH_2 \cdot CHO$ , is a syrupy liquid which decomposes at  $135^\circ$  into crotonaldehyde and water—

$CH_3CH(OH)CH_2 \cdot CHO = CH_3CH : CH \cdot CHO + H_2O$ . It is soluble in water and alcohol, and gives the usual aldehyde reactions.

**Acrolëin**,  $CH_2 : CH \cdot CHO$ , is a pungent-smelling liquid, boiling at  $52-53^\circ$ . It is readily oxidized to acrylic acid.

**Crotonaldehyde**,  $CH_3 \cdot CH : CH \cdot CHO$ , is an extremely disagreeable-smelling liquid boiling at  $104^\circ$ . The oxime melts at  $119-120^\circ$ .


**Benzaldehyde**,  $C_6H_5 \cdot CHO$ , is a pleasant aromatic smelling liquid, which boils at  $179^\circ$ . It does not reduce Fehling's solution but gives most of the aldehyde reactions. Its oxime melts at  $35^\circ$ , the phenylhydrazone at  $155^\circ$ , the semicarbazone at  $214^\circ$ .

**o-Toluic Aldehyde**,  $C_6H_4 \begin{matrix} \swarrow CH_3 \\ \searrow CHO \end{matrix}$ , boils at  $200^\circ$ . Its oxime melts at  $48-49^\circ$ .

**m-Toluic Aldehyde** boils at  $199^\circ$ .

**p-Toluic Aldehyde** is a liquid with a pepper-like odour, boiling at  $204^\circ$ . The oxime exists in two

forms. The anti-derivative melts at  $79^{\circ}$ , the syn-compound at  $109^{\circ}$ .

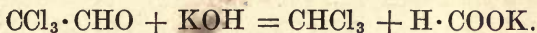
*p*-Cumic Aldehyde, Cuminol,  is a pleasant,  
 $\text{CH}(\text{CH}_3)_2$

aromatic-smelling liquid, boiling at  $237^{\circ}$ . Its oxime melts at  $58^{\circ}$ .

Cinnamic Aldehyde,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CHO}$ , decomposes on boiling. The phenylhydrazone melts at  $168^{\circ}$ .

### SUBSTITUTED ALDEHYDES.

Chloral,  $\text{CCl}_3\cdot\text{CHO}$ , is a colourless, pungent-smelling liquid boiling at  $97\text{--}98^{\circ}$ . Concentrated alkali solutions decompose chloral even at ordinary temperatures into chloroform and alkali formate—



The oxime melts at  $39\text{--}40^{\circ}$ .

Chloral Hydrate,  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ , melts at  $57^{\circ}$ . It is readily soluble in water and alcohol. It does not show the usual aldehyde reactions. By shaking with concentrated sulphuric acid it is immediately converted into chloral.

Bromal,  $\text{CBr}_3\cdot\text{CHO}$ , boils at  $174^{\circ}$ . With alkalis it is decomposed into bromoform and alkali formate.

Bromal Hydrate melts at  $53\text{--}54^{\circ}$ .

*o*-Chlorobenzaldehyde,  $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{Cl} \\ \text{CHO} \end{smallmatrix}$ , is a liquid, boiling at  $213\text{--}214^{\circ}$ , with a strong odour. Its oxime melts at  $75^{\circ}$  (anti), the syn. derivative at  $98\text{--}102^{\circ}$ .

*m*-Chlorobenzaldehyde is obtained in long prisms, melting at 17–18°, boiling at 213°. Oxime, M.P. 70° (syn.).

*p*-Chlorobenzaldehyde is a solid with an odour like benzaldehyde, melting at 47–48°.

*o*-Nitrobenzaldehyde,  $C_6H_4 \begin{smallmatrix} \swarrow CHO \\ \searrow NO_2 \end{smallmatrix}$ , is obtained in the form of long, pale yellow needles, melting at 44°. It has an odour similar to that of benzaldehyde, is readily soluble in alcohol and ether, sparingly in water. Concentrated aqueous sodium hydroxide converts it readily into *o*-nitrobenzoic acid and *o*-nitrobenzylalcohol. The oxime melts at 96°.

*m*-Nitrobenzaldehyde melts at 58°. It is fairly soluble in hot water, readily in alcohol and ether. The oxime melts at 118°.

*p*-Nitrobenzaldehyde melts at 106°. With chromic acid it is converted into its corresponding acid. The oxime melts at 129°.

*o*-Nitrocinnamic aldehyde,  $C_6H_4 \begin{smallmatrix} \swarrow CH:CH:CHO \\ \searrow NO_2 \end{smallmatrix}$ , melts at 127° and is soluble in hot water.

*m*-Nitrocinnamic aldehyde, M.P. 116°.

*p*-Nitrocinnamic aldehyde melts at 141°. The oxime melts at 178–179°.

*o*-Aminobenzaldehyde,  $C_6H_4 \begin{smallmatrix} \swarrow NH_2 \\ \searrow CHO \end{smallmatrix}$ , is obtained in silvery leaflets melting at 39–40°, readily soluble in alcohol and ether, sparingly in water. The acetyl derivative melts at 70°, the oxime at 132°.



*m*-Aminobenzaldehyde is a yellow amorphous substance. The oxime melts at 88°.

*p*-Aminobenzaldehyde melts at 70–71°. The hydrochloride is obtained in red crystals. The acetyl derivative melts at 155°, the oxime at 124°.

Salicylic Aldehyde,  $C_6H_4 \begin{cases} \text{OH} & (1) \\ \text{CHO} & (2) \end{cases}$ , is a pleasant-smelling oil, boiling at 196°. On oxidation it yields salicylic acid. The acetyl derivative melts at 37°, the oxime at 57°.

*m*-Hydroxybenzaldehyde melts at 104°. The aqueous solution is coloured deep violet with ferric chloride solution. The oxime melts at 87°.

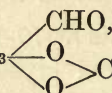
*p*-Hydroxybenzaldehyde melts at 115–116° and sublimes undecomposed. The aqueous solution is coloured faintly violet with ferric chloride. The oxime melts at 65°.

Anisic Aldehyde,  $C_6H_4 \begin{cases} \text{CHO} & (1) \\ \text{OCH}_3 & (4) \end{cases}$ , boils at 248°. The oxime melts at 61°.

Protocatechuic Aldehyde,  $C_6H_3 \begin{cases} \text{CHO} & (1) \\ \text{OH} & (3) \\ \text{OH} & (4) \end{cases}$ , melts at 153°. Ferric chloride colours an aqueous solution of protocatechuic aldehyde green; on addition of sodium carbonate the colour changes to violet and then to red. The oxime melts at 150°.

Vanillin,  $C_6H_3 \begin{cases} \text{CHO} & (1) \\ \text{OCH}_3 & (3) \\ \text{OH} & (4) \end{cases}$  has a pleasant, vanilla-like odour and melts at 80–81°. It gives with ferric

chloride a blue colouration. The benzoate melts at  $75^{\circ}$ , the oxime at  $117^{\circ}$ .

Piperonal,  $C_6H_3$  , has a pleasant helio-

trope odour. It melts at  $37^{\circ}$ . The oxime melts at  $110-112^{\circ}$ , the phenylhydrazone at  $100^{\circ}$ .

Closely related to the aldehydes themselves are the aldehyde ethers. These are liquids, sparingly soluble in water, which on boiling with dilute hydrochloric acid are readily broken up into their constituent aldehyde and alcohol.

Methylal  $CH_2(OCH_3)_2$ , B.P.  $42^{\circ}$ .

Acetal,  $CH_3 \cdot CH(OC_2H_5)_2$ , B.P.  $104^{\circ}$ .

## IX. KETONES.

THE aliphatic ketones are liquids, the common aromatic ketones are solids. They are only oxidized with difficulty and therefore do not reduce alkaline silver solutions. Only those ketones with a methyl group directly attached to the carbonyl group form bisulphite compounds. Like aldehydes they form oximes, phenylhydrazones, and semicarbazones. The methods for the preparation of these derivatives are similar to those employed in the case of the aldehydes.

Acetone,  $CH_3 \cdot CO \cdot CH_3$ , B.P.  $56^{\circ}$ , is miscible with

water in all proportions. With iodine and caustic potash it forms iodoform. The oxime melts at  $59-60^{\circ}$ .

**Methylethylketone**,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_2\text{H}_5$ , boils at  $80-81^{\circ}$ . The oxime is an oil, the semicarbazone melts at  $135-136^{\circ}$ .

**Diethylketone**,  $\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{C}_2\text{H}_5$ , B.P.  $102-103^{\circ}$ .

**Dipropylketone**,  $\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$ , B.P.  $144^{\circ}$ .

**Pinacoline**,  $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} \cdot \text{CO} \cdot \text{CH}_3$ , is a peppermint-smelling liquid boiling at  $106^{\circ}$ . It forms no bisulphite compound. The oxime melts at  $74-75^{\circ}$ .

**Acetophenone**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3$ , melts at  $20^{\circ}$ . With picric acid it gives a picrate, greenish-yellow crystals melting at  $53^{\circ}$ . The oxime melts at  $59^{\circ}$ .

**Benzophenone**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , melts at  $48-49^{\circ}$ . The oxime melts at  $139-140^{\circ}$ , the phenyl-hydrazone at  $137^{\circ}$ .

**Benzoin**,  $\text{C}_6\text{H}_5 \cdot \text{CHOH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , melts at  $137^{\circ}$ . It is converted into benzil by means of nitric acid. Fehling's solution is readily reduced by means of benzoin. The oxime melts at  $151-152^{\circ}$  ( $\alpha$ -derivative).

**Deoxybenzoin**,  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , melts at  $60^{\circ}$ . The oxime melts at  $98^{\circ}$ , the phenylhydrazone at  $116^{\circ}$ .

**Benzil**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , melts at  $95^{\circ}$ . The dioxime melts with decomposition at  $237^{\circ}$ .

## X. ACIDS.

To obtain the acid from a salt, the latter is dissolved in water (if it is insoluble, it is boiled with sodium carbonate and filtered), and the solution acidified. In many cases the acid will be precipitated; if soluble in water it is extracted with ether, the ethereal solution dried and the ether distilled off. The physical and chemical properties of the acid are then determined.

## 1. SATURATED ALIPHATIC MONOBASIC ACIDS.

The lower members are liquids, soluble in water, the solubility decreasing with increase of molecular weight. The higher members are odourless solids, insoluble in water.

**Formic Acid**,  $\text{H}\cdot\text{COOH}$ , when anhydrous boils at  $101^\circ$ . By the action of concentrated sulphuric acid, carbon monoxide is evolved. Formic acid reduces solutions of silver and mercury salts.

**Acetic Acid**,  $\text{CH}_3\cdot\text{COOH}$ , when free from water melts at  $16.5^\circ$ , and boils at  $118^\circ$ . The addition of ferric chloride to a neutral solution of an acetate produces a deep red colour, which on warming disappears, while a brown flocculent precipitate of basic ferric acetate is thrown down.

When acetic acid is warmed with alcohol and concentrated sulphuric acid, ethyl acetate is formed, which may be recognized by its pleasant fruity odour.

**Propionic Acid**,  $\text{C}_2\text{H}_5\cdot\text{COOH}$ , boils at  $141^\circ$ . It is



precipitated as an oil from aqueous solution by the addition of calcium chloride. The ethyl ester boils at 98–99°.

*n*-Butyric Acid,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , boiling at 162°, has an extremely unpleasant odour. Its ethyl ester boils at 120°.

Isobutyric Acid,  $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH}\cdot\text{COOH}$ , boils at 155° and is insoluble in water. The ethyl ester boils at 110°.

Palmitic Acid,  $\text{CH}_3\cdot(\text{CH}_2)_{14}\cdot\text{COOH}$ , melts at 62°. The lead salt formed by adding lead acetate to a neutral solution of ammonium palmitate melts at 112°.

Stearic Acid,  $\text{CH}_3\cdot(\text{CH}_2)_{16}\cdot\text{COOH}$ , melts at 69·2° and the lead salt at 125°.

## 2. SATURATED ALIPHATIC POLYBASIC ACIDS.

These acids are solids, and are soluble in water.

Oxalic Acid,  $\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} + 2\text{H}_2\text{O}$ , melts at 98°. When

acted on by concentrated sulphuric acid, carbon monoxide and carbon dioxide are evolved. Potassium permanganate reacts with oxalic acid, with formation of carbon dioxide and water. The calcium salt is insoluble in water and in acetic acid. The dimethyl ester, which can be prepared by boiling the anhydrous acid with methyl alcohol for about ten minutes, is a solid melting at 54°.

**Malonic Acid**,  $\text{CH}_2 \begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ , melts at  $132^\circ$ . On heating more strongly, it is decomposed into acetic acid and carbon dioxide.

**Succinic Acid**,  $\begin{smallmatrix} \text{CH}_2 \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{COOH} \end{smallmatrix}$ , melts at  $185^\circ$ . When a neutral solution of ferric chloride is added to a neutral solution of a succinate, a brown-red precipitate of basic ferric succinate is produced. Succinic

anhydride  $\begin{smallmatrix} \text{CH}_2\text{CO} \backslash \\ | \\ \text{CH}_2\text{CO} / \end{smallmatrix} \text{O}$  melting at  $119^\circ$ , is obtained by the action of acetyl chloride on the acid at  $50^\circ$ . It is purified by recrystallizing from chloroform.

**Glutaric Acid**,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2\text{COOH} \\ \text{CH}_2\text{COOH} \end{smallmatrix}$ , melting at  $97.5^\circ$ , is converted into the anhydride (M.P.  $56-57^\circ$ ) by heating for some time.

### 3. UNSATURATED ALIPHATIC ACIDS.

**Acrylic Acid**,  $\text{CH}_2\text{:CH}\cdot\text{COOH}$ , boils at  $140^\circ$  and polymerizes. The lead salt crystallizes in fine needles. When acrylic acid is fused with potassium hydroxide, it is decomposed into potassium formate, potassium acetate and hydrogen. The ethyl ester boils at  $101-102^\circ$ .

**Crotonic Acid**,  $\text{CH}_3\cdot\text{CH}\text{:CH}\cdot\text{COOH}$ , melting at  $71-72^\circ$ , when fused with potassium hydroxide produces potassium acetate and hydrogen. Its ethyl ester boils at  $142^\circ$ .

**Oleic Acid**,  $\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CH} : \text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$ , melts at  $14^\circ$ , and boils at  $223^\circ$  at 10 mm. The lead salt is soluble in ether and melts about  $80^\circ$ . When oleic acid is shaken with nitrous acid, it is transformed into the isomeric **Elaïdic Acid**, melting at  $44\text{--}45^\circ$ .

**Fumaric Acid**, 
$$\begin{array}{c} \text{H} - \text{C} - \text{COOH} \\ || \\ \text{HOOC} - \text{C} - \text{H} \end{array}$$
, sublimes at  $200^\circ$ , without melting. When distilled with phosphorus pentoxide, maleic anhydride (M.P.  $60^\circ$ ) is formed. By the action of bromine at  $100^\circ$  on fumaric acid, dibromsuccinic acid, melting at  $255\text{--}256^\circ$  with decomposition, is produced.

**Maleic Acid**, 
$$\begin{array}{c} \text{H} - \text{C} - \text{COOH} \\ || \\ \text{H} - \text{C} - \text{COOH} \end{array}$$
, melting at  $130^\circ$ , is converted into the anhydride (M.P.  $60^\circ$ ) by heating under diminished pressure at  $100^\circ$ .

#### 4. AROMATIC ACIDS.

**Benzoic Acid**,  $\text{C}_6\text{H}_5 \cdot \text{COOH}$ , melts at  $121^\circ$ , and can be sublimed easily. It is practically insoluble in cold water, easily soluble in alcohol and ether. When heated with lime, benzene is produced. Ethyl benzoate (B.P.  $213^\circ$ ), a pleasant-smelling liquid, is easily formed by heating together benzoic acid, ethyl alcohol and a small quantity of concentrated sulphuric acid.

**o-Toluic Acid**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CH}_3 \\ \text{COOH} \end{array}$ , M.P.  $102^\circ$ , is easily

soluble in hot water. Dilute nitric acid oxidizes it to phthalic acid.

*m*-Toluic Acid, M.P.  $110^{\circ}$ , is readily soluble in water.

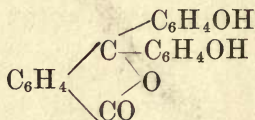
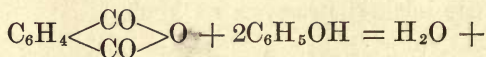
*p*-Toluic Acid, M.P.  $176-177^{\circ}$ . The methyl ester, a strongly smelling solid, melts at  $32^{\circ}$ .

$\alpha$ -Naphthoic Acid,  $C_{10}H_7 \cdot COOH$ , M.P.  $160^{\circ}$  and

$\beta$ -Naphthoic Acid, M.P.  $182^{\circ}$  are converted into naphthalene by distillation with lime. When the  $\alpha$ -compound is oxidized with chromic acid in glacial acetic acid, phthalic acid is produced. Methyl  $\beta$ -naphthoate is a solid melting at  $77^{\circ}$ .

Phthalic Acid,  $C_6H_4 \begin{matrix} \swarrow COOH (1) \\ \searrow COOH (2) \end{matrix}$ , on heating forms

phthalic anhydride (M.P.  $128^{\circ}$ ). When the latter is heated with phenol and a little anhydrous zinc chloride, phenolphthalein is produced—



Phenylacetic Acid,  $C_6H_5 \cdot CH_2 \cdot COOH$ , M.P.  $76^{\circ}$ , is sparingly soluble in cold water.

Hydrocinnaminic Acid,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH$ , M.P.  $48^{\circ}$ .

Cinnamic Acid,  $C_6H_5 \cdot CH : CH \cdot COOH$ , M.P.  $133^{\circ}$ . The methyl ester melts at  $33^{\circ}$ .

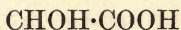


## 5. SUBSTITUTED ACIDS.

## A. HYDROXY ACIDS.

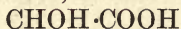
**Glycollic Acid**,  $\text{CH}_2\text{OH} \cdot \text{COOH}$ , melting at  $78-79^\circ$ , when heated to  $100^\circ$  is converted into an anhydride, M.P.  $128-130^\circ$ .

**Lactic Acid**,  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{COOH}$ , is a syrup, easily soluble in water and alcohol, difficultly soluble in ether. Hydriodic Acid reduces it to propionic acid, while at the same time free iodine is produced. The silver salt melts at  $100^\circ$ .



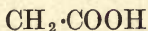
**Malic Acid**,  $\begin{array}{c} | \\ \text{CH}_2 \cdot \text{COOH} \end{array}$ , melts at  $100^\circ$ . When

calcium chloride and alcohol are added to a neutral solution of a malate, calcium malate is precipitated.

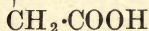


**Tartaric Acid**,  $\begin{array}{c} | \\ \text{CHOH} \cdot \text{COOH} \end{array}$ , melting at  $168-170^\circ$ ,

is decomposed on heating strongly, with production of a smell of burnt sugar. Calcium chloride added to a neutral solution of a tartrate (but not of tartaric acid) precipitates calcium tartrate. When ammoniacal silver nitrate solution is added to a neutral solution of a tartrate, a silver mirror is produced on warming.



**Citric Acid**,  $\begin{array}{c} | \\ \text{C}(\text{OH}) \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{COOH} \end{array} + \text{H}_2\text{O}$ , is easily soluble



in water and alcohol. It loses its water of crystalliz-

ation at  $130^{\circ}$ , and melts at  $153^{\circ}$ . When calcium chloride is added to a neutral solution of a citrate and the mixture heated for some time, calcium citrate is precipitated.

**Salicylic Acid**,  $C_6H_4 \begin{matrix} \swarrow OH \\ \searrow COOH \end{matrix} \begin{matrix} (1) \\ (2) \end{matrix}$ , melting at  $155^{\circ}$ , is converted into phenol when it is heated with lime. Ferric chloride added to a solution of salicylic acid produces a deep violet colouration, which is not destroyed by addition of acetic acid. Methyl salicylate, which has a characteristic odour, boils at  $224^{\circ}$ .

**Protocatechuic Acid**,  $C_6H_3 \begin{matrix} \swarrow OH \\ \searrow OH \\ \searrow COOH \end{matrix} \begin{matrix} (1) \\ (2) \\ (4) \end{matrix}$ , melts at  $199^{\circ}$ .

Ferric chloride added to a solution of the acid, produces a green colouration, which, on addition of sodium hydroxide, changes to blue and finally to red.

**Gallic Acid**,  $C_6H_2(OH)_3 \cdot COOH + H_2O$ , decomposes at  $220^{\circ}$ , into carbon dioxide and pyrogallol (see page 26). Ferric chloride produces a blue-black precipitate, soluble in hydrochloric acid but reprecipitated by ammonia.

**Tannic Acid** is an amorphous powder, more soluble in water than in alcohol. Ferric chloride solution added to a solution of the acid, produces a blue-black colouration. When sulphuric acid is added to a concentrated solution of tannic acid, a white precipitate is formed, which in contact with air turns blue.

**Mandelic Acid**,  $C_6H_5 \cdot CHOH \cdot COOH$ , melts at  $118^{\circ}$ ,

and is easily soluble in water. Oxidation with nitric acid produces benzaldehyde. The methyl ester melts at  $52^{\circ}$ .

## B. HALOGEN SUBSTITUTED ACIDS.

**Monochloroacetic Acid**,  $\text{CH}_2\text{Cl}\cdot\text{COOH}$ , melting at  $62\text{--}63^{\circ}$ , heated with caustic potash forms glycollic acid.

**Dichloroacetic Acid**,  $\text{CHCl}_2\cdot\text{COOH}$ , is a liquid, boiling at  $189\text{--}191^{\circ}$ .

**Trichloroacetic Acid**,  $\text{CCl}_3\cdot\text{COOH}$ , melts at  $55^{\circ}$ . When digested with caustic potash, chloroform and potassium carbonate are formed.

**Monobromoacetic Acid**,  $\text{CH}_2\text{Br}\cdot\text{COOH}$ , melts at  $49\text{--}50^{\circ}$ .

**Dibromoacetic Acid**,  $\text{CHBr}_2\cdot\text{COOH}$  melts at  $48^{\circ}$ .

**Tribromoacetic Acid**,  $\text{CBr}_3\cdot\text{COOH}$  melts at  $135^{\circ}$ .

***o*-Chlorobenzoic Acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{Cl} \\ \diagdown \\ \text{COOH} \end{matrix}$ , M.P.  $137^{\circ}$ .

Reduction with sodium amalgam produces benzoic acid.

***m*-Chlorobenzoic Acid**, M.P.  $153^{\circ}$ .

***p*-Chlorobenzoic Acid**, M.P.  $236^{\circ}$ .

***o*-Bromobenzoic Acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{Br} \\ \diagdown \\ \text{COOH} \end{matrix}$ , M.P.  $147^{\circ}$ .

***m*-Bromobenzoic Acid**, M.P.  $155^{\circ}$ .

***p*-Bromobenzoic Acid**, M.P.  $251^{\circ}$ .

When the halogen benzoic acids are distilled with lime, the corresponding halogen derivatives of benzene are produced.

## C. NITRO ACIDS.

*o*-Nitrobenzoic Acid,  $C_6H_4 \begin{smallmatrix} \swarrow NO_2 \\ \searrow COOH \end{smallmatrix}$ , M.P. 147°.

*m*-Nitrobenzoic Acid, M.P. 141°.

*p*-Nitrobenzoic Acid, M.P. 238°.

These acids can be reduced to the corresponding amino-acids by tin and hydrochloric acid.

*o*-Nitrocinnamic Acid,  $C_6H_4 \begin{smallmatrix} \swarrow NO_2 \\ \searrow CH : CH \cdot COOH \end{smallmatrix}$ ,

M.P. 237-240°.

*m*-Nitrocinnamic Acid, light yellow needles. M.P. 197°.

*p*-Nitrocinnamic Acid, M.P. 286°.

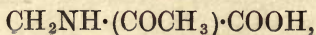
Oxidation with alkaline potassium permanganate solution converts these acids into the corresponding nitrobenzaldehyde and nitrobenzoic acid.

## D. AMINO ACIDS.

**Aminoacetic Acid** (glycine),  $CH_2NH_2 \cdot COOH$ , M.P. 232°, with decomposition, is converted by nitrous acid into glycollic acid. Ferric chloride added to a solution of glycine causes an intense red colouration which is discharged by acids, and restored by ammonia.

**Methyl Glycine** (sarcosine),  $CH_2NH(CH_3) \cdot COOH$ , M.P. 210-215°, gives by the action of nitrous acid a nitroso-compound. When heated with soda-lime, sarcosine produces methylamine.

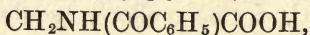
**Aceturic Acid** (Acetoglycine),



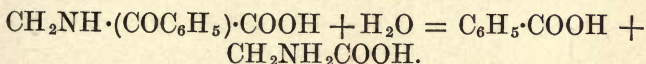


melts at  $206^{\circ}$ . On boiling with acids, it is decomposed into glycine and acetic acid.

**Hippuric Acid** (Benzoylglycine),



melting at  $187^{\circ}$ , is decomposed by boiling with dilute acids into benzoic acid and glycine.



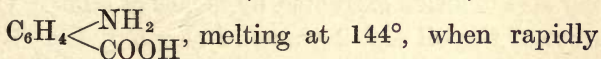
**Aminopropionic Acid** (Alanine)  $\text{CH}_3 \cdot \text{CHNH}_2 \cdot \text{COOH}$ .

When heated with concentrated phosphoric acid solution it is decomposed into carbon dioxide, ammonia and acetaldehyde.

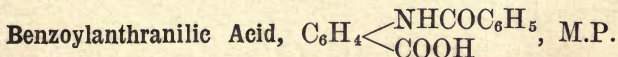
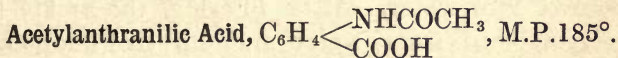
**Aspartic Acid**,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$ . Nitrous acid converts it into malic acid.

**Asparagine**,  $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$ , forming large rhombic crystals, decomposes over  $200^{\circ}$  without melting. When heated with alkalis, ammonia and aspartic acid are produced. With nitrous acid it gives malic acid.

**o-Aminobenzoic Acid** (Anthranilic Acid),



heated, decomposes into carbon dioxide and aniline. Nitrous acid transforms it into salicylic acid.



$177^{\circ}$ .

**m-Aminobenzoic Acid** forms small reddish crystals, M.P.,  $173-174^{\circ}$ ,

*p*-Aminobenzoic Acid, M.P. 186–187°.

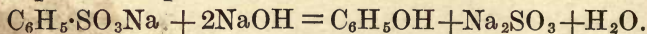
*o*-Aminocinnamic Acid,  $C_6H_4 \begin{matrix} \searrow NH_2 \\ \swarrow CH : CH \cdot COOH \end{matrix}$ ,  
M.P. 158–159°, forms yellow needles and gives  
fluorescent solutions in ether and alcohol.

## XI. AROMATIC SULPHONIC ACIDS.

THESE are, as a rule, very soluble in water and crystallize with difficulty. To identify them, it is best to prepare the sulphonamide and take its melting point. The sodium salts are easily obtained by salting out.

PREPARATION OF THE AMIDE.—One gram of the sodium salt and 2 grams phosphorus pentachloride are heated on a water bath. After the reaction is finished, the mixture is poured into water and the oily acid chloride extracted by means of ether. One gram of the oil and 2 grams of ammonium carbonate are heated on a water bath until the smell of the chloride disappears. The reaction product is then poured into water. After filtering, the amide is recrystallized from water and its melting-point determined.

When a sulphonic acid or a salt is fused with alkali, a phenol is produced—



METHOD.—One gram of the acid or salt is mixed

with 2 grams solid caustic potash and heated in a nickel crucible to about  $200^{\circ}$  for one hour. After cooling the product is dissolved in water, the solution acidified and the phenol extracted with ether and identified.

By passing superheated steam into the sulphonic acid, a hydrocarbon results.

**Benzene sulphonic acid**,  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ , M.P.  $50^{\circ}$ . M.P. of amide,  $150^{\circ}$ .

***o*-Toluene sulphonic acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_3 \\ \text{SO}_3\text{H} \end{matrix} \cdot 2\text{H}_2\text{O}$ , deliquescent leaflets. M.P. of amide,  $155^{\circ}$ .

***m*-Toluene sulphonic acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_3 \\ \text{SO}_3\text{H} \end{matrix} \cdot \text{H}_2\text{O}$ , deliquescent needles. M.P. of amide,  $107^{\circ}$ .

***p*-Toluene Sulphonic acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_3 \\ \text{SO}_3\text{H} \end{matrix} \cdot 4\text{H}_2\text{O}$ , crystallizes in leaflets. M.P.  $92^{\circ}$ . M.P. of amide,  $137^{\circ}$ .

***o*-Benzene disulphonic acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{SO}_3\text{H} \\ \text{SO}_3\text{H} \end{matrix}$ , M.P. of chloride,  $105^{\circ}$ ; of amide,  $233^{\circ}$ .

***m*-Benzene disulphonic acid**, M.P. of chloride,  $53^{\circ}$ ; of amide,  $228^{\circ}$ .

***p*-Benzene disulphonic acid**, M.P. of chloride,  $131^{\circ}$ ; of amide,  $288^{\circ}$ .

***o*-Phenolsulphonic acid**,  $\text{C}_6\text{H}_4\begin{matrix} \text{OH} \\ \text{SO}_3\text{H} \end{matrix} \cdot \frac{3}{4}\text{H}_2\text{O}$ , melts above  $50^{\circ}$ . When the potassium salt is treated with benzoyl chloride, potassium chloride is precipitated, and on extraction with ether, phenyl benzoate is obtained.

*m*-Phenolsulphonic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \text{SO}_3\text{H} \end{smallmatrix} \cdot 2\text{H}_2\text{O}$ , crystallizes in fine needles. Ferric chloride produces in solutions of the acid, a violet colouration.

*p*-Phenolsulphonic Acid is oxidized by manganese dioxide and sulphuric acid to quinone. When boiled with hydriodic acid, *p*-phenolsulphonic acid is decomposed into phenol and sulphuric acid.

*o*-Chlorobenzenesulphonic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{Cl} \\ \text{SO}_3\text{H} \end{smallmatrix}$ , The chloride melts at  $28.5^\circ$ ; the amide at  $188^\circ$ .

*m*-Chlorobenzenesulphonic acid. The chloride is an oil; the amide melts at  $148^\circ$ .

*p*-Chlorobenzenesulphonic acid. M.P. of chloride,  $53^\circ$ ; of amide,  $143^\circ$ .

*o*-Bromobenzenesulphonic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{Br} \\ \text{SO}_3\text{H} \end{smallmatrix}$ . M.P. of chloride,  $51^\circ$ ; of amide,  $186^\circ$ .

*m*-Bromobenzenesulphonic acid. The chloride is oily. M.P. of amide,  $154^\circ$ .

*p*-Bromobenzenesulphonic acid, melts at  $88^\circ$ . M.P. of chloride,  $75^\circ$ ; of amide,  $166^\circ$ .

*o*-Iodobenzenesulphonic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{I} \\ \text{SO}_3\text{H} \end{smallmatrix}$ . M.P. of chloride,  $51^\circ$ ; of amide,  $170^\circ$ .

*p*-Iodobenzenesulphonic acid. The chloride melts at  $86-87^\circ$ ; the amide at  $183^\circ$ .

*o*-Nitrobenzenesulphonic Acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NO}_2 \\ \text{SO}_3\text{H} \end{smallmatrix}$ . M.P. of chloride,  $67^\circ$ ; of amide,  $186^\circ$ .

*m*-Nitrobenzenesulphonic acid. M.P. of chloride,  $60.5^\circ$ ; of amide,  $161^\circ$ .



*p*-Nitrobenzenesulphonic acid. The chloride is oily ; the amide melts at  $181^{\circ}$ .

*p*-Aminobenzenesulphonic acid (Sulphanilic acid),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH}_2 \\ \text{SO}_3\text{H} \end{smallmatrix}$ , when oxidized gives quinone. Fusion with caustic potash produces aniline and not aminophenol.

*o*-Sulphobenzoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_3\text{H} \\ \text{COOH} \end{smallmatrix}$ , when anhydrous melts at  $250^{\circ}$ . On fusion with caustic potash it is converted into salicylic acid. The imino derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2 \\ \text{CO} \end{smallmatrix} \text{NH}$ , known as Saccharin, melts with partial decomposition at  $220^{\circ}$ . By heating with alkalis, saccharin is decomposed into ammonia and *o*-sulphobenzoic acid. The sodium salt,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2 \\ \text{CO} \end{smallmatrix} \text{NNa}$  (the saccharin of commerce) is readily soluble in water.

$\alpha$ -Naphthalene sulphonic acid,  $\text{C}_{10}\text{H}_7\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ , M.P.  $85-90^{\circ}$ . The chloride crystallizes from ether in leaflets, melting at  $66^{\circ}$ . The amide melts at  $150^{\circ}$ . Potassium permanganate in acid solution oxidizes the sulphonic acid to phthalic acid.

$\beta$ -Naphthalene sulphonic acid, M.P.  $161^{\circ}$ . The chloride melts at  $76^{\circ}$ ; the amide at  $212^{\circ}$ .

## XII. ACID ANHYDRIDES.

THE aliphatic acid anhydrides are mostly colourless liquids, insoluble in water, readily soluble in alcohol and ether, with boiling points higher than those of the corresponding acids. The aromatic acid anhydrides are solids with melting-points lower than those of the corresponding acids. Water slowly hydrolyses anhydrides with formation of acids. With alkalis they readily form salts of the corresponding acids, and with alcohols, esters are produced.

**Acetic anhydride**,  $(\text{CH}_3\text{CO})_2\text{O}$ , B.P.  $137-138^\circ$ .

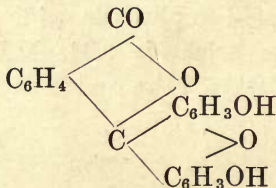
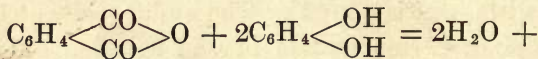
**Succinic Anhydride**,  $\begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{CH}_2\text{CO} \end{array} \text{O}$ , M.P.  $119-120^\circ$ ,

reverts to the acid in moist air.

**Benzoic anhydride**,  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ , M.P.  $42^\circ$ .

**Phthalic anhydride**,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ , melts at  $128^\circ$

and sublimes readily in long needles. When fused with resorcinol, fluorescein is produced (*see* p. 26).



## XIII. ACID HALIDES.

THESE are pungent-smelling liquids, readily converted by water into the acid, or by alkali into the salt of the acid.

Acetyl chloride,  $\text{CH}_3\cdot\text{COCl}$ , B.P.  $55^\circ$ .

Acetyl bromide, B.P.  $81^\circ$ .

Acetyl iodide, B.P.  $108^\circ$ .

Propionyl chloride,  $\text{C}_2\text{H}_5\cdot\text{COCl}$ , B.P.  $80^\circ$ .

Propionyl bromide, B.P.  $104^\circ$ .

Propionyl iodide, B.P.  $127\text{--}128^\circ$ .

Malonyl chloride,  $\text{CH}_2 \begin{array}{l} \diagup \text{COCl} \\ \diagdown \text{COCl} \end{array}$ , B.P.  $58^\circ$ .

Succinyl chloride,  $\begin{array}{c} \text{CH}_2\cdot\text{COCl} \\ | \\ \text{CH}_2\cdot\text{COCl} \end{array}$ , B.P.  $190\text{--}192^\circ$ .

Benzoyl chloride,  $\text{C}_6\text{H}_5\cdot\text{COCl}$ , B.P.  $198^\circ$ .

Benzoyl bromide, B.P.  $218\text{--}219^\circ$ .

Phthalyl chloride,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COCl} \\ \diagdown \text{COCl} \end{array}$ , B.P.  $275^\circ$ .

## XIV. ACID AMIDES.

THESE are well crystallized substances with definite melting points. They are, as a general rule, less soluble in water than the ammonium salts of the corresponding acids. When heated with alkalies, they give ammonia and the salt of the acid. With

nitrous acid they yield nitrogen and the corresponding acid.

**Acetamide**,  $\text{CH}_3\cdot\text{CONH}_2$ , M.P.  $82-83^\circ$ .

**Propionamide**,  $\text{C}_2\text{H}_5\cdot\text{CONH}_2$ , M.P.  $79^\circ$ .

**Acetobromamide**,  $\text{CH}_3\cdot\text{CONHBr} + \text{H}_2\text{O}$ , M.P.  $70-80^\circ$ , when boiled with caustic potash gives potassium bromide, carbon dioxide and methylamine. The anhydrous compound melts at  $108^\circ$ .

**Oxamide**,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$ , sublimes on heating. It is insoluble in water and in alcohol.

**Oxamic acid**,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{COOH} \end{array}$ , M.P.  $210^\circ$  with decomposition.

**Oxamethane**,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}$ , M.P.  $114-115^\circ$ , when boiled with caustic potash yields ammonia, ethyl alcohol and potassium oxalate.

**Succinamide**,  $\begin{array}{c} \text{CH}_2\cdot\text{CONH}_2 \\ | \\ \text{CH}_2\cdot\text{CONH}_2 \end{array}$ , at  $200^\circ$  is converted into the imide and ammonia.

**Cyanamide**,  $\text{CN}\cdot\text{NH}_2$ , M.P.  $40^\circ$ , with copper sulphate gives a black compound, copper cyanamide,  $\text{CN}_2\text{Cu}$ .<sup>1</sup>

**Benzamide**,  $\text{C}_6\text{H}_5\cdot\text{CONH}_2$ , M.P.  $128^\circ$ , is soluble in hot water, alcohol and ether.

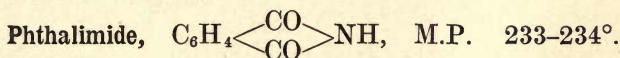
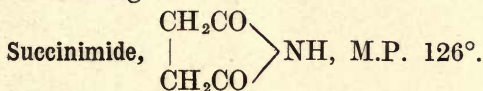
<sup>1</sup> Calcium cyanamide  $\text{CN}_2\text{Ca}$  is a commercial product. On addition of water, ammonia is evolved.



**Phthalic Diamide**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CONH}_2 \\ \diagdown \text{CONH}_2 \end{smallmatrix}$ , on heating changes to phthalimide with loss of ammonia.

## XV. ACID IMIDES.

THE imides, like the acid amides, are hydrolysed by boiling with alkalis. The only common imides are the following :—



Alcoholic caustic potash precipitates the potassium salt,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \rangle \text{NK}$ , from a solution of phthalimide in alcohol. This salt is insoluble in alcohol and ether, and sparingly soluble in water.

## XVI. ACID ANILIDES.

THESE are hydrolysed by heating with concentrated hydrochloric acid or alkali and the aniline distilled with steam from an alkaline solution. The acid is then identified in the non-volatile residue.

**Formanilide**,  $\text{H} \cdot \text{CONHC}_6\text{H}_5$ , melting at  $46^\circ$ , is

readily soluble in water, alcohol and ether. With concentrated caustic soda solution there is produced a crystalline sodium compound,  $\text{H} \cdot \text{CONaC}_6\text{H}_5$ .

**Acetanilide** (antifebrin)  $\text{CH}_3 \cdot \text{CONHC}_6\text{H}_5$ , M.P.  $112^\circ\text{H}$

$\text{COOH}$

**Oxanilic acid**,  $\text{CONHC}_6\text{H}_5 \cdot \text{H}_2\text{O}$ , M.P. (anhydrous)

$\text{CONHC}_6\text{H}_5$

149–150°.

$\text{CONHC}_6\text{H}_5$

**Oxanilide**,  $\text{CONHC}_6\text{H}_5$ , M.P.  $245^\circ$ .

$\text{CONHC}_6\text{H}_5$

**Benzanilide**,  $\text{C}_6\text{H}_5 \cdot \text{CONHC}_6\text{H}_5$ , M.P.  $161\text{--}162^\circ$ .

## XVII. ESTERS.

THESE are mostly pleasant-smelling, volatile liquids, insoluble in water. (Methyl oxalate and methyl tartrate are solids.)

A small quantity of the ester is hydrolysed with 10 per cent. alkali solution, under a reflux condenser. Two-thirds of the liquid are distilled over, dehydrated with potassium carbonate and examined for the alcohol. The residue in the distilling flask contains the alkali salt of the acid.

**Formates** -methyl, B.P.  $32.5^\circ$ .

-ethyl, B.P.  $54.5^\circ$ .

-propyl, B.P.  $82\text{--}83^\circ$ .

-butyl, B.P.  $107^\circ$ .

-*n*-amyl, B.P.  $130.5^\circ$ .

Acetates -methyl, B.P.  $57.5^{\circ}$ .

-ethyl, B.P.  $77^{\circ}$ .

-propyl, B.P.  $101^{\circ}$ .

-butyl, B.P.  $125^{\circ}$ .

-isobutyl, B.P.  $116^{\circ}$ .

-*n*-amyl, B.P.  $148^{\circ}$ .

Glycol monoacetate, B.P.  $182^{\circ}$ .

Glycol diacetate, B.P.  $186-187^{\circ}$ .

Glycerol triacetate, B.P.  $258-259^{\circ}$ .

Propionates-methyl, B.P.  $79.5^{\circ}$ .

-ethyl, B.P.  $99^{\circ}$ .

Butyrates-methyl, B.P.  $102.3^{\circ}$ .

-ethyl, B.P.  $120^{\circ}$ .

Oxalates-dimethyl, M.P.  $54^{\circ}$ .

-diethyl, B.P.  $186^{\circ}$ .

Malonates-dimethyl, B.P.  $181-182^{\circ}$ .

-diethyl, B.P.  $198^{\circ}$ .

Succinates-dimethyl, M.P.  $18^{\circ}$ , B.P.  $195^{\circ}$ .

-ethyl, B.P.  $216^{\circ}$ .

Malates-dimethyl, B.P.  $122^{\circ}$  at 12 mm.

-diethyl, B.P.  $129^{\circ}$  at 12 mm.

-*n*-dipropyl, B.P.  $150^{\circ}$  at 12 mm.

Ethereal malates on heating under ordinary pressure decompose into the corresponding fumarates.

Tartrates -dimethyl, M.P.  $48^{\circ}$ .

-diethyl, B.P.  $280^{\circ}$ .

-*n*-dipropyl, B.P.  $303^{\circ}$ .

Benzoates -methyl, B.P.  $199^{\circ}$ .

-ethyl, B.P.  $213^{\circ}$ .

-*n*-propyl, B.P.  $229^{\circ}$ .

Glycol di-benzoate, M.P.  $73^{\circ}$ .

Glycerol tri-benzoate, M.P.  $76^{\circ}$ .

Salicylates -methyl, B.P.  $224^{\circ}$ .

-ethyl, B.P.  $231.5^{\circ}$ . When distilled with barium oxide ethyl phenyl ether is produced.

-phenyl (salol), M.P.  $42-43^{\circ}$ .

Phthalates -dimethyl, B.P.  $282^{\circ}$ .

-diethyl, B.P.  $288^{\circ}$ .

-diphenyl, M.P.  $70^{\circ}$ .

Cinnamates -methyl, M.P.  $36^{\circ}$ , B.P.  $260^{\circ}$ .

-ethyl, B.P.  $271^{\circ}$ .

phenyl, M.P.  $72^{\circ}$ . On distillation in air, carbon dioxide and stilbene are formed.

## XVIII. QUINONES.

THESE compounds are characterized by their colour (yellow or red), peculiar odour and volatility in steam. With the exception of anthraquinone and phenanthraquinone, they are readily reduced by sulphur dioxide to the corresponding dihydric phenols.

**Benzoquinone** (quinone),  $C_6H_4O_2$ , M.P.  $116^{\circ}$ , is soluble in water. With phenol, quinone forms phenoquinone,  $C_6H_4O_2 \cdot 2C_6H_5OH$ , crystallizing in red needles, melting at  $71^{\circ}$ . Phenoquinone is turned



blue by caustic potash, green by barium hydroxide. Quinone liberates iodine from potassium iodide.

*o*-Quinone forms bright red crystals. It has no smell and is not volatile. It is reduced by sulphurous acid to catechol.

$\alpha$ -Naphthoquinone,  $C_{10}H_6O_2$ , M.P.  $125^\circ$ , is yellow and on oxidation with nitric acid, forms phthalic acid.

$\beta$ -Naphthoquinone decomposes about  $120^\circ$ . It crystallizes in red needles. It is odourless and non-volatile.

Anthraquinone,  $C_{14}H_8O_2$ , M.P.  $273^\circ$ , when treated with zinc dust and caustic soda, produces oxanthranol,

$C_6H_4 \begin{smallmatrix} \text{CHOH} \\ \text{CO} \end{smallmatrix} C_6H_4$ , which is red. The latter

compound is easily oxidized on standing in air, anthraquinone being again formed.

Phenanthraquinone, M.P.  $205^\circ$ , is not reduced by sulphur dioxide. It dissolves in concentrated sulphuric acid to a dark green solution. When ignited with zinc dust, phenanthraquinone gives phenanthrene. The monoxime  $C_{14}H_8O:NOH$  melts at  $158^\circ$ .

Chloranil (tetrachlorquinone),  $C_6Cl_4O_2$ , forms golden-yellow leaflets, with a smell reminiscent of Harris tweed. It sublimes undecomposed. With caustic potash it forms the purple potassium chloranilate,  $C_6Cl_2(OK)_2O_2$ . By the addition of acid to the latter, chloranilic acid, which crystallizes in reddish scales, is liberated.

## XIX. CARBOHYDRATES.

THESE are solids, which, with the exception of starch, are soluble in water.

*d*-Glucose (dextrose),  $C_6H_{12}O_6 \cdot H_2O$ , M.P.  $86^\circ$ . The anhydrous compound melts at  $145^\circ$ . Glucose reduces Fehling's solution. Glucosazone melts at  $204\text{--}205^\circ$ . Glucose pentabenzoate melts at  $179^\circ$ .

PREPARATION OF THE OSAZONE.—One gram of the sugar is dissolved in 5 cc. water, and 4 grams phenylhydrazine in 5 grams glacial acetic acid are added. The solution is heated on a water-bath for about ten minutes, when the osazone separates in yellow crystals. These are dried and the melting-point determined. This should be done quickly as the osazone decomposes to some extent in the neighbourhood of the melting-point.

Galactose, M.P.  $163\text{--}164^\circ$ . The osazone melts at  $193\text{--}194^\circ$ .

Fructose (laevulose), M.P.  $95^\circ$ . With phenylhydrazine it gives *d*-glucosazone. The pentabenzoate melts at  $78\text{--}79^\circ$ .

Cane Sugar,  $C_{12}H_{22}O_{11}$ , melting at  $160^\circ$ , does not reduce Fehling's solution. When boiled with dilute acids, glucose and fructose are produced. It forms no osazone. With benzoyl chloride it gives a hexabenzoate, melting at  $109^\circ$ .

Lactose (Milk sugar),  $C_{12}H_{22}O_{11} \cdot H_2O$ , becomes anhydrous at  $140^\circ$ , and melts with decomposition

at 205°. The osazone melts at 200°. Lactose reduces Fehling's solution.

Maltose,  $C_{12}H_{22}O_{11} \cdot H_2O$ , loses water at 100°. When boiled with dilute acids, glucose is formed. The osazone melts at 190–191°.

Starch  $(C_6H_{10}O_5)_n$ , with iodine gives a blue colour, which disappears on heating. Starch is hydrolysed by heating with dilute acids, forming glucose. On boiling with water starch swells up and partially dissolves.

## XX. GLUCOSIDES.

THESE, on hydrolysis with dilute acids or alkalies, give a sugar—generally glucose—and other substances.

Myronic Acid,  $C_{10}H_{19}O_{10}NS_2$ , usually occurs as the potassium salt. When boiled with barium hydroxide it is decomposed into glucose, allyl isothiocyanate (*see* p. 92) and potassium hydrogen sulphate.

Arbutin,  $C_6H_4 \begin{matrix} \diagup OC_6H_{11}O_5 \\ \diagdown OH \end{matrix} \begin{matrix} (1) \\ (4) \end{matrix}$ , is soluble in water.

When ferric chloride is added to the aqueous solution, the latter is turned deep blue. On hydrolysis with dilute sulphuric acid, glucose and hydroquinone are produced.

Salicin,  $C_6H_4 \begin{matrix} \diagup OC_6H_{11}O_5 \\ \diagdown CH_2OH \end{matrix} \begin{matrix} (1) \\ (2) \end{matrix}$ , melting at 201°, on

hydrolysis gives glucose and saligenin. Concentrated sulphuric acid produces a deep red colour. It is oxidized by chromic acid mixture to carbon dioxide, formic acid and salicyl aldehyde.

Amygdalin,  $C_{20}H_{27}O_{11}N, 3H_2O$ , loses water at  $120^\circ$ , melting at  $200^\circ$  and is hydrolysed by dilute acids into glucose, benzaldehyde and hydrocyanic acid.

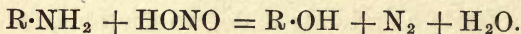
Helicin,  $C_6H_4 \begin{matrix} \diagup OC_6H_{11}O_5 \\ \diagdown CHO \end{matrix}, \frac{3}{4}H_2O$ , loses water at  $100^\circ$  and melts at  $175^\circ$ . On hydrolysis with dilute acids it gives glucose and salicyl aldehyde.

## XXI. AMINES.

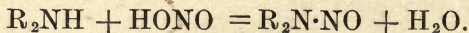
### ALIPHATIC AMINES.

THE lower members are inflammable gases possessing an ammoniacal odour and are readily soluble in water, while the higher members are liquids. With acids they form salts which are soluble in water and in alcohol.

Nitrous Acid converts *primary* amines into the corresponding alcohols, with evolution of nitrogen—



*Secondary* amines are converted into yellow nitrosoamines—

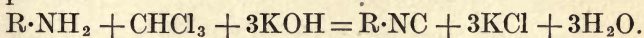


*Tertiary* amines are unacted upon.



**METHOD.**—A small quantity of the amine is dissolved in dilute hydrochloric acid, care being taken that an excess of acid is present. To the cooled solution, a solution of sodium nitrite is added until free nitrous acid is present (starch iodine test).

*Primary* amines are also distinguished by giving the carbylamine test with chloroform and alcoholic potash—



**METHOD.**—About 0.1 gram of the amine is mixed with 3 drops chloroform and about 2 cc. alcoholic potash solution, and gently heated. A disgusting smell of carbylamine is evolved.

**N.B.**—The lower aliphatic amines are usually met with as salts.

**Methylamine Hydrochloride**,  $CH_3NH_2 \cdot HCl$ , forms deliquescent crystals.

**Ethylamine**,  $C_2H_5NH_2$ , B.P.  $18-19^\circ$ . The hydrochloride melts at  $76-80^\circ$ .

**Diethylamine**,  $(C_2H_5)_2NH$ , B.P.  $56^\circ$ . M.P. of hydrochloride  $215-217^\circ$ .

**Triethylamine**,  $(C_2H_5)_3N$ , B.P.  $89^\circ$ .

**Propylamine**,  $(C_3H_7)NH_2$ , B.P.  $49^\circ$ . The hydrochloride melts at  $157-158^\circ$ .

**Isopropylamine**,  $(CH_3)_2CHNH_2$ , B.P.  $31-32^\circ$ . The hydrochloride is deliquescent.

*n*-Butylamine,  $C_4H_9NH_2$ , B.P.  $76^\circ$ .

*n*-Amylamine,  $C_5H_{11}NH_2$ , B.P.  $103^\circ$ .

**Allylamine**,  $CH_2 : CH \cdot CH_2NH_2$ . B.P.  $56^\circ$ .

**Ethylenediamine**,  $C_2H_4(NH_2)_2$ , B.P.  $116^\circ$ . Nitrous acid converts it into ethylene oxide.

**Tetramethylenediamine** (putrescine),  $C_4H_8(NH_2)_2$ ,  
M.P. 27–28°.

**Pentamethylene Diamine** (cadaverine),  $C_5H_{10}(NH_2)_2$ .  
B.P. 178–179°.

### AROMATIC AMINES.

These are liquids or solids, and behave in many respects like the aliphatic amines. The *primary* compounds give the carbylamine reaction.

**ACTION OF NITROUS ACID.**—If the amino group is in the *nucleus* there are formed in cold acid solution diazonium salts, which on heating evolve nitrogen and produce phenols. If to a solution of a diazonium salt  $\beta$ -naphthol in caustic soda is added, a coloured precipitate of an azo-compound appears.

**PREPARATION OF A DIAZONIUM SALT.**—The amine is dissolved in a large excess of dilute hydrochloric acid and cooled in ice-water. Sodium nitrite solution is added in small quantities at a time, the mixture being well shaken after each addition, until, after standing for a few minutes, free nitrous acid can be detected by starch-iodide paper.

If the amino group is in the *side chain*, no diazonium salt is formed, and the amine behaves like the aliphatic compounds.

With *secondary* aromatic amines, nitroso-derivatives are formed, as in the case of aliphatic compounds.

Dialkylanilines with nitrous acid form para-nitroso compounds, the free bases of which are usually green, while the hydrochlorides are orange-coloured.

To completely identify an aromatic amine, its acetyl compound is prepared and its melting-point determined.

**METHOD.**—To 1 gram of the amine is added 1 gram acetic anhydride. The solid acetyl compound usually separates immediately. It is recrystallized from water or alcohol and its melting-point taken.

**Aniline**,  $\text{C}_6\text{H}_5\text{NH}_2$ , B.P.  $182-183^\circ$ . A chip of pine wood dipped first in hydrochloric acid and then in aniline, is turned yellow. Bleaching powder solution, when shaken with aniline becomes violet. On diazotizing and warming, aniline is converted into phenol. Acetanilide melts at  $112^\circ$ .

**Methylaniline**,  $\text{C}_6\text{H}_5\text{NHCH}_3$ , B.P.  $193-194^\circ$ , forms a nitroso-derivative,  $\text{C}_6\text{H}_5\text{NCH}_3\cdot\text{NO}$ , M.P.  $12-15^\circ$ . The acetyl derivative melts at  $101-102^\circ$ .

**Dimethylaniline**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , boils at  $195^\circ$ . The para-nitroso compound, which can be separated from its salts by means of sodium carbonate and extraction with ether, forms green crystals of metallic appearance, melting at  $85^\circ$ .

**Ethylaniline**,  $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_5$ , B.P.  $206^\circ$ . The acetyl derivative melts at  $54.5^\circ$ .

**Diethylaniline**,  $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$ , B.P.  $213-214^\circ$ . *p*-Nitroso-compound M.P.  $84^\circ$ .

**Diphenylamine**,  $(\text{C}_6\text{H}_5)_2\text{NH}$ , melts at  $54^\circ$  and has a pleasant odour. The nitroso-derivative melts at  $66.5^\circ$ .

**Triphenylamine**,  $(\text{C}_6\text{H}_5)_3\text{N}$ , M.P.  $127^\circ$ . With concentrated sulphuric acid, there is produced a violet colouration, which changes to green.

***o*-Toluidine**,  $C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix}$ , boils at  $197^\circ$ . Ferric chloride precipitates a blue compound from its solution in hydrochloric acid. The acetyl compound melts at  $110^\circ$ .

***m*-Toluidine**, B.P.  $202^\circ$ . The acetyl compound melts at  $65^\circ$ .

***p*-Toluidine**, M.P.  $45^\circ$ . The melting point of the acetyl compound is  $153^\circ$ .

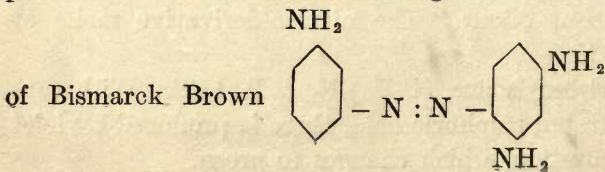
***α*-Naphthylamine**,  $C_{10}H_7NH_2$ , M.P.  $50^\circ$ . On oxidation with chromic acid, *α*-naphthaquinone is produced.

***β*-Naphthylamine**, M.P.  $111-112^\circ$ . Potassium permanganate oxidizes it to phthalic acid.

**Benzylamine**,  $C_6H_5 \cdot CH_2NH_2$ , B.P.  $183-185^\circ$  is strongly alkaline.

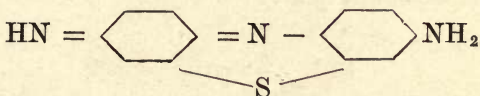
***o*-Phenylenediamine**,  $C_6H_4 \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ , M.P.  $102^\circ$ . When ferric chloride is added to the hydrochloric acid solution, a dark red colouration is produced, and there quickly separate red needles of diamidophenazine  $C_6H_4 \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} C_6H_2 (NH_2)_2$ . The di-acetyl compound of *o*-phenylenediamine melts at  $185-186^\circ$ .

***m*-Phenylenediamine**, M.P.  $63^\circ$ . Dilute nitrous acid produces a brown colouration owing to the formation





*p*-Phenylenediamine, M.P.  $147^{\circ}$ . When about 0.1 gram is dissolved in dilute hydrochloric acid and a little sulphuretted hydrogen water added along with a few drops of ferric chloride solution, and the mixture warmed, there appears a deep violet colouration (the so-called Lauth violet),



**Benzidine**,  $\text{NH}_2\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{NH}_2$  melting at  $122^{\circ}$ , forms silvery leaflets, easily soluble in hot water and alcohol. The sulphate is insoluble in water.

### HALOGEN AMINES.

*o*-Chloroaniline,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{Cl} \\ \diagup \text{NH}_2 \end{smallmatrix}$ , B.P.  $207^{\circ}$ . The acetyl compound melts at  $87-88^{\circ}$ .

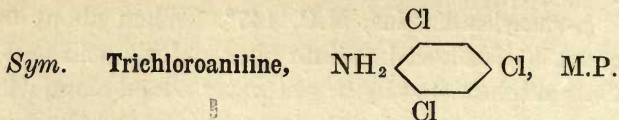
*m*-Chloroaniline, B.P.  $230^{\circ}$ . M.P. of acetyl compound,  $72.5^{\circ}$ .

*p*-Chloroaniline, M.P.  $70^{\circ}$ . M.P. of acetyl compound,  $172.5^{\circ}$ .

*o*-Bromoaniline,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{Br} \\ \diagup \text{NH}_2 \end{smallmatrix}$ , M.P.  $31^{\circ}$ . M.P. of acetyl compound,  $99^{\circ}$ .

*m*-Bromoaniline, M.P.  $18^{\circ}$ , B.P.  $251^{\circ}$ . M.P. of acetyl compound,  $87.5^{\circ}$ .

*p*-Bromoaniline, M.P.  $63^{\circ}$ . M.P. of acetyl compound,  $167-168^{\circ}$ .



77.5°. M.P. of acetyl compound, 204°.

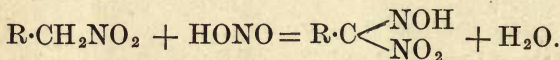
*Sym.* Tribromoaniline, M.P. 119–120°. M.P. of acetyl compound, 232°.

## XXII. NITRO-COMPOUNDS.

### ALIPHATIC NITRO-COMPOUNDS.

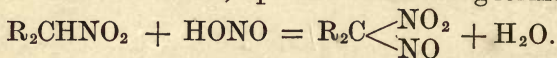
THESE are agreeably-smelling liquids, soluble in water. Many of them dissolve in alkalies.

**ACTION OF NITROUS ACID.**—With a *primary* aliphatic nitro-compound nitrous acid produces a red colouration due to the formation of a *nitrolic acid*.



The potassium salt is red.

With a *secondary* compound there is produced a dark blue colouration, a pseudo-nitrol being formed—



*Tertiary* compounds are unacted upon by nitrous acid.

**METHOD.**—A small quantity of the compound is shaken in a test-tube with sufficient caustic soda to form a clear solution. A few drops of a solution of sodium nitrite are added and finally dilute sulphuric

acid drop by drop. In the case of a primary compound excess of acid destroys the red colouration, which, however, is restored by addition of caustic soda.

**REDUCTION.**—Nitro-compounds are readily reduced to amines.

**METHOD.**—A few pieces of granulated zinc are placed on a test-tube and covered with caustic potash solution. Two cc. of the nitro-compound are introduced and the mixture warmed. The amine will be observed by its smell and its action on red litmus paper.

**Nitromethane**,  $\text{CH}_3\text{NO}_2$ , B.P.  $101^\circ$ . Alcoholic caustic soda precipitates the sodium compound,  $\text{CH}_2\text{:NO}_2\text{Na}$ . Concentrated hydrochloric acid decomposes it with formation of formic acid.

**Nitroethane**,  $\text{C}_2\text{H}_5\text{NO}_2$ , B.P.  $114\text{--}115^\circ$ . Concentrated hydrochloric acid converts it into acetic acid.

**Nitropropane**,  $\text{C}_3\text{H}_7\text{NO}_2$ , B.P.  $130\text{--}131^\circ$ .

**Tertiary Nitrobutane**,  $(\text{CH}_3)_3\text{CNO}_2$ , is crystalline, melting at  $24^\circ$ . It is insoluble in alkalies.

### AROMATIC NITRO-COMPOUNDS.

These are generally yellow oils or solids, insoluble in water, dilute hydrochloric acid or dilute caustic soda solution. Di-nitro and tri-nitro compounds impart a deep yellow colour to caustic soda solution.

They are reduced to amines by acid reducing agents.

**METHOD.**—A small quantity of the nitro-compound

is treated with zinc dust and hydrochloric acid, heat being applied if necessary. The mixture is diluted and rendered alkaline with caustic soda. It is then extracted with ether and the amine identified.

**Nitrobenzene**,  $C_6H_5NO_2$ , B.P.  $209^\circ$ , is a yellow oil with an odour of bitter almonds. On reduction it yields aniline.

***o*-Nitrotoluene**,  $C_6H_4\begin{smallmatrix} \text{CH}_3 \\ \text{NO}_2 \end{smallmatrix}$ , boils at  $218^\circ$ . It gives *o*-toluidine on reduction.

***m*-Nitrotoluene**, melts at  $16^\circ$ , and boils at  $230\text{--}231^\circ$ .

***p*-Nitrotoluene**, M.P.  $54^\circ$ .

***o*-Dinitrobenzene**,  $C_6H_4\begin{smallmatrix} \text{NO}_2 \\ \text{NO}_2 \end{smallmatrix}$ , M.P.  $117\text{--}118^\circ$ . On reduction it gives *o*-phenylenediamine.

***m*-Dinitrobenzene**, M.P.  $91^\circ$ .

***p*-Dinitrobenzene**, M.P.  $171\text{--}172^\circ$ .

**$\alpha$ -Nitronaphthalene**,  $C_{10}H_7NO_2$ , melting at  $61^\circ$ , on reduction yields  $\alpha$ -naphthylamine and with chromic acid is oxidized to nitrophthalic acid.

**$\beta$ -Nitronaphthalene**, M.P.  $79^\circ$ , gives on reduction  $\beta$ -naphthylamine.

### NITROPHENOLS.

These compounds, on reduction with tin and hydrochloric acid, yield aminophenols.

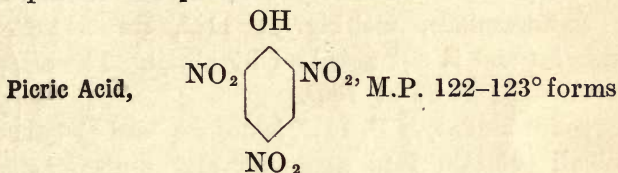
***o*-Nitrophenol**,  $C_6H_4\begin{smallmatrix} \text{NO}_2 \\ \text{OH} \end{smallmatrix}$ , melting at  $44^\circ$ , has an intense yellow colour and a peculiar odour. It is



easily volatile in steam. The sodium salt gives a red solution in water.

*m*-Nitrophenol, M.P.  $96^{\circ}$ , forms sulphur-yellow crystals.

*p*-Nitrophenol, M.P.  $114^{\circ}$ , forms colourless needles which turn pink on exposure to air. The potassium salt is yellow. Phosphorus pentachloride converts the phenol into *p*-chloronitrobenzene, M.P.  $83^{\circ}$ .



yellow leaflets soluble in hot water. With aromatic hydrocarbons crystalline molecular compounds are obtained (see Naphthalene, p. 17). When picric acid is warmed with a concentrated solution of potassium cyanide, a dark red solution of isopurpuric acid is produced.

### NITROKETONES.

*o*-Nitroacetophenone,  $C_6H_4NO_2CO \cdot CH_3$ , is an oil with a peculiar smell. It is oxidized by potassium permanganate to *o*-nitrobenzoic acid.

*m*-Nitroacetophenone forms needles melting at  $80-81^{\circ}$ . The oxime melts at  $131^{\circ}$ .

*p*-Nitroacetophenone, crystallizes in yellow prisms, melting at  $80-81^{\circ}$ .

### NITROANILINES.

These are solids, yellow or orange in colour. They

have basic properties and are soluble in acids. On reduction with tin and hydrochloric acid the corresponding diamines are produced.

*o*-Nitroaniline,  $C_6H_4 \begin{smallmatrix} \diagup NO_2 \\ \diagdown NH_2 \end{smallmatrix}$ , crystallizes in orange-yellow needles, melting at  $71^\circ$ . When boiled with alkali it loses ammonia with production of *o*-nitrophenol. The acetyl derivative melts at  $92^\circ$ .

*m*-Nitroaniline, melting at  $114^\circ$ , forms yellow needles and is not acted on by alkali. The acetyl compound melts at  $150^\circ$ .

*p*-Nitroaniline, M.P.  $147^\circ$ , is decomposed by boiling alkali solution into ammonia and *p*-nitrophenol. The acetyl compound melts at  $207^\circ$ .

Picramide,  $NO_2 \begin{array}{c} NH_2 \\ | \\ \text{C}_6\text{H}_2 \\ | \\ NO_2 \end{array} NO_2$ , forms orange-red

needles melting at  $188^\circ$ . When heated with alkali, alkali picrate is formed, and ammonia is evolved.

### XXIII. NITROSO-COMPOUNDS.

Nitrosobenzene,  $C_6H_5NO$ , M.P.  $68^\circ$ , when fused or in solution has an intense greenish-blue colour.

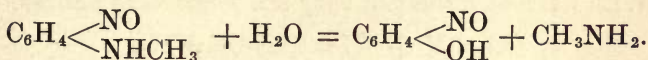
*p*-Nitrosoaniline,  $C_6H_4 \begin{smallmatrix} \diagup NO \\ \diagdown NH_2 \end{smallmatrix}$ , forms steel-blue

needles, melting at  $174^{\circ}$ . On boiling with caustic soda, it forms ammonia and *p*-nitrosophenol.

*p*-Nitrosophenol,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{NO} \\ \text{OH} \end{smallmatrix}$ , M.P.  $126^{\circ}$ , is slightly

soluble in water, giving a light green solution. It is reduced by tin and hydrochloric acid to *p*-aminophenol. Concentrated nitric acid oxidizes it to *p*-nitrophenol.

Methyl-*p*-nitrosoaniline,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{NO} \\ \text{NHCH}_3 \end{smallmatrix}$  (1), forms large crystals with metallic lustre, M.P.  $118^{\circ}$ . When boiled with caustic soda solution, it is decomposed into nitrosophenol and methylamine.



*p*-Nitrosodimethylaniline,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{NO} \\ \text{N}(\text{CH}_3)_2 \end{smallmatrix}$ , forms green crystals, melting at  $85^{\circ}$ . The hydrochloride is yellow and is soluble with difficulty in water. Dilute caustic soda solution on warming decomposes the base into *p*-nitrosophenol and dimethylamine. It does not give Liebermann's nitroso reaction.

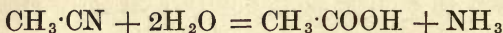
*α*-Nitrosonaphthol (*α*-naphthoquinone oxime),  $\text{C}_{10}\text{H}_6(\text{OH})(\text{NO})$  1 : 4, forms needles melting with decomposition at  $193\text{--}194^{\circ}$ .

*β*-Nitrosonaphthol (*β*-naphthoquinone oxime),  $\text{C}_{10}\text{H}_6(\text{OH})(\text{NO})$  1 : 2, crystallizes in yellowish-green needles, melting with decomposition at  $152^{\circ}$ . It dissolves in concentrated sulphuric acid with an intense red colour. When a neutral solution of the

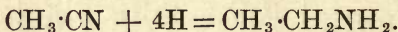
sodium salt of  $\beta$ -nitroso-naphthol is added to a cobalt salt solution, a brown-red precipitate is formed.

## XXIV. NITRILES AND ISONITRILES.

THE nitriles are liquids or solids of low melting-point, and have an agreeable odour. When boiled with strong mineral acids they are hydrolysed into the corresponding acids—



With nascent hydrogen they are reduced to amines.



**HYDROLYSIS OF NITRILES.**—Two cc. of the substance are boiled for some time with about 20 cc. concentrated hydrochloric acid. The liquid is then rendered alkaline with caustic soda and heated.

The residual liquid is tested for the fatty acid.

**REDUCTION OF NITRILES.**—One cc. of the substance is treated with 10 cc. dilute hydrochloric acid and a little zinc dust. The solution is rendered alkaline with caustic soda, and the amine identified.

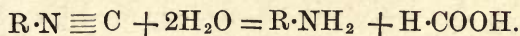
**Acetonitrile**,  $\text{CH}_3\cdot\text{CN}$ . is a colourless liquid, boiling at  $81-82^\circ$ .

**Benzonitrile**,  $\text{C}_6\text{H}_5\cdot\text{CN}$ , B.P.  $191^\circ$ , is an oil with the odour of bitter almonds.

**Isonitriles** or **Carbylamines** are not usually met with unless in testing for primary amines. They are

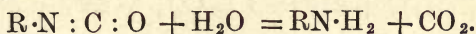


liquids possessing a disgusting odour. On hydrolysis with acids they yield formic acid and an amine.



## XXV. ISOCYANATES.

THESE are liquids, which, when digested with caustic potash yield primary amines and potassium carbonate, and with acids, a salt of a primary amine and carbon dioxide—



Methyl Isocyanate, B.P. 44°.

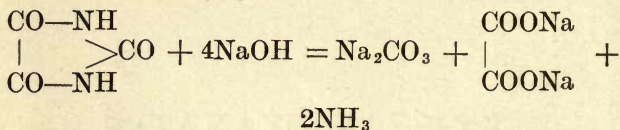
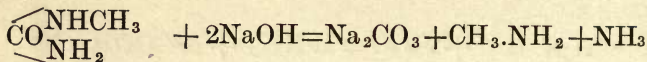
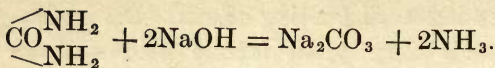
Ethyl Isocyanate, B.P. 60°.

Allyl Isocyanate, B.P. 82°.

Phenyl Isocyanate, B.P. 165–166°.

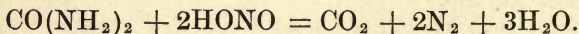
## XXVI. UREAS AND UREIDES.

WHEN ureas and alkyl ureas are digested with caustic soda solution sodium carbonate remains, while from the former ammonia is evolved, from the latter amines. In the case of ureides, ammonia or amines may be given off, and the residue consists of sodium carbonate and the sodium salt of the acid of the ureide.

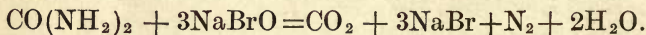


Urea,  $\begin{array}{c} \diagup \text{NH}_2 \\ \text{CO} \\ \diagdown \text{NH}_2 \end{array}$ , M.P. 132–133°, is a colourless solid.

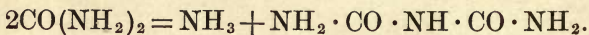
When treated with nitrous acid it is decomposed into nitrogen and carbon dioxide—



With a solution of sodium hypobromite it gives the same decomposition products—



**BIURET REACTION.**—When urea is heated above its melting-point, ammonia is evolved and a residue of biuret remains—



When the biuret is dissolved in water and copper sulphate added and then caustic potash drop by drop, a violet colouration appears.

Methylurea,  $\begin{array}{c} \diagup \text{NHCH}_3 \\ \text{CO} \\ \diagdown \text{NH}_2 \end{array}$ , crystallizes in prisms,

melting at 102°. On heating for some time it decomposes into ammonia, methylamine and the dimethyl ester of cyanuric acid, which melts at 222°.

Ethylurea,  $\text{CO} \begin{array}{l} \diagup \text{NHC}_2\text{H}_5 \\ \diagdown \text{NH}_2 \end{array}$ , melts at  $92^\circ$ . It decom-

poses on heating, into ammonia, ethylamine and the diethyl ester of cyanuric acid, M.P.  $173^\circ$ .

Parabanic Acid (Oxalylurea),  $\text{CO}-\text{NH} \begin{array}{l} \diagup \text{CO} \\ \diagdown \text{CO}-\text{NH} \end{array}$ , on

heating with caustic potash solution gives potassium oxalate, potassium carbonate and ammonia.

Barbituric Acid (Malonylurea),  $\text{CO} \begin{array}{l} \diagup \text{NHCO} \\ \diagdown \text{NHCO} \end{array} \text{CH}_2$ , on

heating with caustic potash solution yields potassium malonate, potassium carbonate and ammonia.

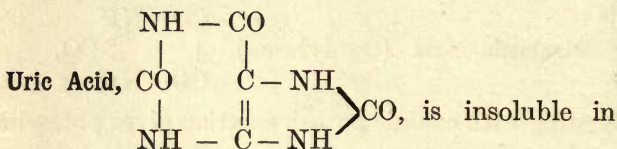
Alloxan (Mesoxalylurea),  $\text{CO} \begin{array}{l} \diagup \text{NHCO} \\ \diagdown \text{NHCO} \end{array} \text{CO}$ , has an

acid reaction. Ferrous sulphate gives a deep blue colour to the solution. When alloxan is boiled with dilute nitric acid, it is decomposed into parabanic acid and carbon dioxide.

Guanidine,  $\text{CNH} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{NH}_2 \end{array}$ , is a deliquescent strongly

basic substance. The nitrate, M.P.  $214^\circ$ , dissolves with difficulty in water. When boiled with alkalis, guanidine is decomposed giving ammonia and alkali carbonate.

## XXVII. URIC ACID GROUP.



alcohol, and practically insoluble in water.

1. When the acid is heated with soda lime ammonia is evolved.

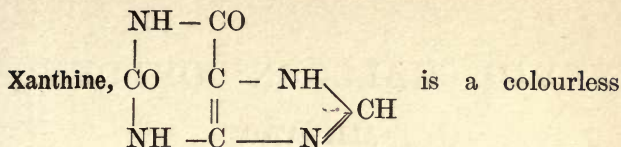
2. **MUREXIDE TEST.**—A small quantity of the acid is moistened with concentrated nitric acid, and the mixture evaporated to dryness in a porcelain basin on a water-bath. There remains a reddish residue, which on addition of dilute ammonia solution changes to purple red, while alkali produces a violet colouration.

3. Fehling's solution is reduced by uric acid.

4. If a little of the acid be dissolved in a drop of caustic soda solution and this placed on filter paper which has been moistened with a solution of silver nitrate, a dark brown spot of metallic silver is immediately produced.

5. On dry distillation, uric acid decomposes without melting, giving off ammonia and hydrocyanic acid.

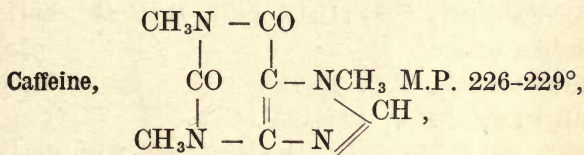




powder, soluble with difficulty in water, but very easily soluble in alkalies.

When a small quantity of xanthine is warmed with freshly-made chlorine water and a trace of nitric acid until evolution of gas ceases, the solution then carefully evaporated to dryness, and the solid exposed to ammonia gas, a rose-red colour is produced.

If xanthine be evaporated with nitric acid (Sp. Gr. 1.4), the residue is yellow. On addition of caustic potash it becomes yellowish red, and on warming violet-red.



is fairly soluble in water and in alcohol.

When evaporated with concentrated nitric acid it gives the murexide test (*see Uric Acid*).

When caffeine is evaporated with chlorine water, it leaves a purple red residue, which on strongly heating becomes yellow, but on addition of ammonia is changed to red.

## XXVIII. HALOGEN COMPOUNDS.

## ALIPHATIC.

THE alkyl halides are liquids which have a high specific gravity, and are practically insoluble in water. They are hydrolysed to the corresponding alcohols by warming with an excess of alkali solution.

Ethyl bromide,  $C_2H_5Br$ , B.P.  $39^\circ$ .

*n*-Propyl bromide,  $C_3H_7Br$ , B.P.  $71^\circ$ .

Isopropyl bromide,  $CH_3 \cdot CHBr \cdot CH_3$ , B.P.  $59-60^\circ$ .

Methyl iodide, B.P.  $43^\circ$ .

Ethyl iodide, B.P.  $72^\circ$ .

Propyl iodide, B.P.  $102^\circ$ .

Isopropyl iodide, B.P.  $89.5^\circ$ .

Allyl chloride,  $CH_2 : CH \cdot CH_2Cl$ , B.P.  $46^\circ$ , has a leek-like odour.

Allyl bromide, B.P.  $70-71^\circ$ .

Allyl iodide, B.P.  $102-103^\circ$ .

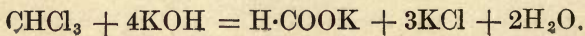
Methylene iodide,  $CH_2I_2$ , boils at  $180^\circ$  with partial decomposition.

Ethylene chloride,  $CH_2Cl \cdot CH_2Cl$ , B.P.  $84^\circ$ .

Ethylene bromide, B.P.  $131-132^\circ$ .

Ethylene iodide, melts at  $81-82^\circ$ .

Chloroform,  $CHCl_3$ , B.P.  $61.5^\circ$ , is a colourless non-inflammable liquid. When boiled with alcoholic caustic potash, potassium formate and potassium chloride are formed—

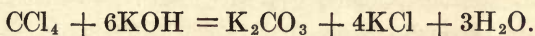


The carbylamine test may also be applied (see page 11).

**Bromoform**,  $\text{CHBr}_3$ , B.P.  $151^\circ$ .

**Iodoform**,  $\text{CHI}_3$ , M.P.  $119\text{--}120^\circ$ , crystallizes in brilliant yellow leaflets of a characteristic odour.

**Carbon tetrachloride**,  $\text{CCl}_4$ , B.P.  $76\text{--}77^\circ$ , is a pleasant smelling liquid. When treated with zinc and hydrochloric acid, it is reduced to chloroform. On heating with alcoholic potash it is decomposed into potassium carbonate and potassium chloride.



## AROMATIC HALOGEN COMPOUNDS

are divided into two classes :—

1. True aromatic halogen compounds, i.e. those with the halogen attached to the benzene nucleus.

2. Those with the halogen in the side chain.

The members of the first class are colourless liquids or solids, with a faint, agreeable odour. They are insoluble in water, but readily soluble in the other common solvents. They easily form nitro-derivatives. Caustic alkali does not readily remove the halogen from these compounds.

**Monochlorobenzene**,  $\text{C}_6\text{H}_5\text{Cl}$ , B.P.  $132^\circ$ .

*o*-**Dichlorobenzene**,  $\text{C}_6\text{H}_4\text{Cl}_2$ , B.P.  $179^\circ$ .

*m*-**Dichlorobenzene**, B.P.  $172^\circ$ .

*p*-**Dichlorobenzene**, M.P.  $53^\circ$ .

**Monobromobenzene**,  $\text{C}_6\text{H}_5\text{Br}$ , B.P.  $156\text{--}157^\circ$ .

*o*-**Dibromobenzene**,  $\text{C}_6\text{H}_4\text{Br}_2$ , B.P.  $224^\circ$ .

*m*-**Dibromobenzene**, B.P.  $219^\circ$ .

*p*-Dibromobenzene, M.P. 89°.

Iodobenzene,  $C_6H_5I$ , B.P. 188°.

*o*-Chlorotoluene,  $C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \text{Cl} \end{smallmatrix}$ , B.P. 156°.

*m*-Chlorotoluene, B.P. 150°.

*p*-Chlorotoluene, B.P. 163°.

*o*-Bromotoluene,  $C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \text{Br} \end{smallmatrix}$ , B.P. 181°.

*m*-Bromotoluene, B.P. 183–184°.

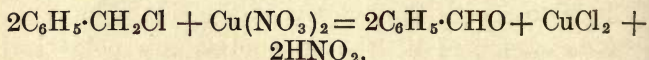
*p*-Bromotoluene, M.P. 28–29°.

$\alpha$ -Chloronaphthalene,  $C_{10}H_7Cl$ , B.P. 263°.

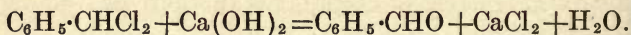
$\beta$ -Chloronaphthalene, M.P. 56°, B.P. 265°.

The compounds with halogen in the side chain behave like aliphatic halogen compounds.

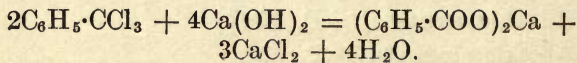
**Benzyl chloride**,  $C_6H_5 \cdot CH_2Cl$ , B.P. 175°, when boiled with a solution of copper nitrate, benzaldehyde is formed—



**Benzal chloride** (benzylidene chloride),  $C_6H_5 \cdot CHCl_2$ , B.P. 206°, forms benzaldehyde, when heated with milk of lime—



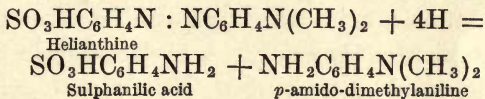
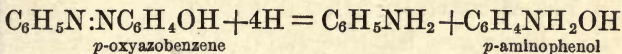
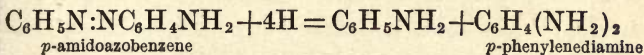
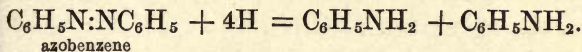
**Benzotrichloride**,  $C_6H_5 \cdot CCl_3$ , B.P. 213°, on heating with milk of lime, gives calcium benzoate—





## XXIX. AZO COMPOUNDS.

THESE compounds are coloured solids, which on reduction produce amino compounds.



METHOD OF REDUCTION.—About 3 grams of the compound are warmed with zinc dust and water until the colour has disappeared. The mixture is then extracted with ether and the ethereal solution evaporated to dryness. The residue may be :—

1. A mixture of two amines.
2. A mixture of an amine and an aminophenol.
3. A mixture of an amine and an aminosulphonic acid.

MIXTURE OF TWO AMINES.—The residue of liquid is distilled and the first and last fractions treated with acetic anhydride. The acetyl compounds thus formed are then identified by their melting points.

MIXTURE OF AN AMINE AND AN AMINOPHENOL.—The aminophenol is extracted from the mixture with alkali.

**MIXTURE OF AN AMINE AND AN AMINOSULPHONIC ACID.**—The mixture is neutralized with alkali, the amine extracted with ether, and identified. The aminosulphonic acid is liberated by adding hydrochloric acid to the alkali salt.

**Azobenzene**,  $C_6H_5N : NC_6H_5$ , M.P.  $68^\circ$ , is easily soluble in alcohol. When treated with tin and hydrochloric acid, benzidine is produced.

***p*-Aminoazobenzene**,  $C_6H_5N : NC_6H_4NH_2$ , forms yellow leaflets melting at  $125$ – $126^\circ$ . It is oxidized by sulphuric acid and manganese dioxide with formation of quinone. The hydrochloride crystallizes in steel-blue needles. The acetyl derivative melts at  $142^\circ$ .

**Diaminoazobenzene**,  $C_6H_5N : NC_6H_3 \begin{matrix} \swarrow NH_2 & (1) \\ \searrow NH_2 & (3) \end{matrix}$

forms yellow needles, M.P.  $117^\circ$ . On reduction it yields aniline and triaminobenzene, M.P.  $132^\circ$ . The hydrochloride of diaminoazobenzene is known as **chrysoïdine**.

**Triaminoazobenzene**,  $NH_2C_6H_4N : NC_6H_3 \begin{matrix} \swarrow NH_2 & (2) \\ \searrow NH_2 & (4) \end{matrix}$ ,  
M.P.  $143^\circ$ .

**Helianthine**,  $SO_3HC_6H_4N : NC_6H_4N(CH_3)_2$ , forms glistening violet leaflets. On reduction it yields sulphanilic acid and *p*-amino-dimethylaniline, M.P.  $41^\circ$ . The sodium salt is known as **Methyl Orange**.

The following, which are related to the azo-compounds, should also be mentioned.

**Hydrazobenzene**,  $C_6H_5NH \cdot NHC_6H_5$ , M.P.  $131^\circ$ , forms colourless leaflets, which are insoluble in water.

If its alcoholic solution be exposed to air, azobenzene is produced. Powerful reducing agents decompose it into aniline.

Azoxybenzene,  $\text{C}_6\text{H}_5\text{N} - \text{NC}_6\text{H}_5$ , crystallizes in long

$\text{O}$

yellow needles, M.P.  $36^\circ$ . It is insoluble in water. On distillation it decomposes into azobenzene and aniline.

Diazoaminobenzene,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{NHC}_6\text{H}_5$ , melts at  $96^\circ$  and explodes at higher temperatures.

### XXX. PYRIDINE AND QUINOLINE GROUP.

Pyridine,  $\text{C}_5\text{H}_5\text{N}$ , B.P.  $116^\circ$ , has a strong characteristic odour, and is miscible in all proportions with water, alcohol and ether. It forms salts with acids. On reduction with sodium and alcohol, piperidine is produced.

Piperidine,  $\text{C}_5\text{H}_{11}\text{N}$ , B.P.  $106^\circ$ , is a colourless liquid with a characteristic odour. It is miscible with water, alcohol and ether. It is a secondary amine.

Quinoline,  $\text{C}_9\text{H}_7\text{N}$ , B.P.  $239^\circ$ , is sparingly soluble in water. The hydrochloride is crystalline. With methyl iodide quinoline forms a yellow crystalline compound melting at  $72^\circ$ .

## XXXI. ALKALOIDS.

THE alkaloids are nearly all solids, easily soluble in alcohol, soluble with difficulty in ether, chloroform and benzene, and sparingly soluble or insoluble in water. Most are optically active, generally laevo-rotatory. They dissolve readily in dilute acids with formation of salts, from which the alkaloid is precipitated on addition of an alkali. Morphine, however, is soluble in excess of sodium hydroxide.

The following reactions are given by almost all the alkaloids :—

1. When an alkaloid is heated in a dry test-tube, decomposition takes place with production of a smell like burning feathers.

2. A solution of iodine in potassium iodide produces a brown flocculent precipitate in solutions of salts of the alkaloids, best when acidified with dilute sulphuric acid.

3. Phosphomolybdic acid<sup>1</sup> produces a yellow precipitate in solutions of all the alkaloids. The precipitate is soluble in alkalies and alkaline carbonates.

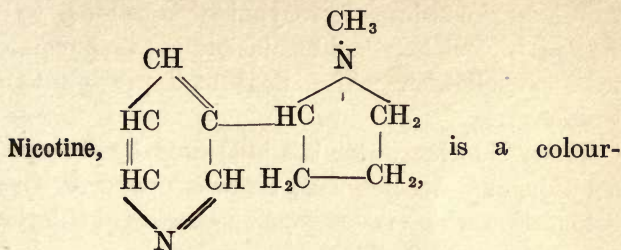
4. Potassium mercuric iodide<sup>2</sup> produces a white or yellowish white precipitate in solutions of salts of alkaloids. The precipitates are insoluble in dilute hydrochloric acid.

5. Aqueous solutions of tannic acid and of picric acid precipitate all or nearly all the alkaloids from solutions of their salts.

<sup>1</sup> See Appendix.

<sup>2</sup> See Appendix.





less oil with an unpleasant smell, B.P. 247°.

Picric acid produces an amorphous precipitate which readily crystallizes in small yellow needles melting at 218°.

Quinine, when anhydrous melts at 177°. The normal salts are sparingly soluble, the acid salts very soluble.

Solutions of quinine salts, when acidified with sulphuric acid show a fine blue fluorescence.

Concentrated sulphuric acid dissolves the alkaloid to a colourless solution, which on heating turns brown and yellow.

When a solution of a quinine salt is mixed with one-fifth of its volume of chlorine water and then with an excess of ammonia, an emerald green colour is produced. If a little potassium ferrocyanide solution be added after the chlorine water and then a few drops of ammonia, the solution becomes deep red in colour.

**Cinehonine, M.P. 250°.**

When chlorine water and an excess of ammonia are added to a solution of a cinchonine salt, a yellowish white precipitate is formed.

When potassium ferrocyanide is added to a neutral or slightly acid solution of a cinchonine salt, a yellowish white flocculent precipitate is produced.

When chlorine water is added drop by drop to a solution of a brucine salt, there is produced a red colouration which is destroyed by excess of chlorine.

**Strychnine**, M.P. 284°.

If a crystal of potassium dichromate be stirred in a solution of the alkaloid in concentrated sulphuric acid, there appears a fine blue colour, which changes successively to violet, red and reddish yellow.

Potassium ferricyanide and also potassium chromate produce yellow crystalline precipitates in neutral and fairly concentrated solutions of strychnine salts.

**Brucine**, when anhydrous melts at 178°.

The solution in concentrated sulphuric acid has at first a rose-red colour, which changes to yellow.

Concentrated nitric acid dissolves brucine and its salts giving an intensely red solution, which, when warmed, turns yellow. If stannous chloride be added to this yellow solution, an intense violet colouration is produced.

**Morphine** is soluble in dilute acids and in alkalies. Its salts dissolve easily in water and alcohol.

The addition of concentrated nitric acid to the solid alkaloid or a salt causes a yellowish red colour to appear.

When ammonium molybdate in concentrated

sulphuric acid (0.1 gram in a cc.) is placed in a porcelain dish and a particle of morphine added and crushed with a glass rod, a deep violet colour appears, which slowly changes to blue.

If a few drops of a dilute neutral solution of ferric chloride be added to a concentrated solution of a morphine salt, a dark blue colouration is produced. The colour is destroyed by acids.

**Narcotine**, M.P. 176°.

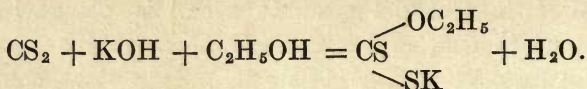
Cold concentrated sulphuric acid dissolves the alkaloid, giving a yellow solution. If this be carefully heated in a porcelain dish, the colour changes from yellow through orange to red, while a bluish violet colour appears at the edges. If the heating be continued until the acid begins to evaporate, the solution acquires a reddish violet colour.

If to a solution of narcotine in concentrated sulphuric acid there be added 10 to 20 drops sulphuric acid containing a trace of nitric acid, the liquid turns brown and then quickly red.

## XXXII. SULPHUR COMPOUNDS.

(OTHER THAN SULPHONIC ACIDS AND DERIVATIVES.)

**Carbon Disulphide**,  $\text{CS}_2$ , is a highly refractive colourless liquid boiling at 47°. When it is added to alcoholic potash, potassium xanthate is precipitated in yellow needles—



### MERCAPTANS OR THIO-ALCOHOLS.

These are colourless liquids with a disagreeable garlic-like odour, and are insoluble in water.

1. Oxidation with nitric acid produces sulphonic acids which can be identified by conversion into their amides (*see* page 48).

2. When a mercaptan is added to a few cc. of an alcoholic solution of mercuric chloride, a white precipitate is formed.

3. When sodium is added to a mercaptan in ethereal solution, hydrogen is evolved and the sodium salt crystallizes in white needles.

Ethyl mercaptan,  $\text{C}_2\text{H}_5\text{SH}$ , B.P.  $36^\circ$ .

*n*-Propyl mercaptan,  $\text{C}_3\text{H}_7\text{SH}$ , B.P.  $68^\circ$ .

Isopropyl mercaptan,  $(\text{CH}_3)_2\text{CHSH}$ , B.P.  $59^\circ$ .

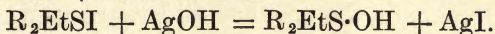
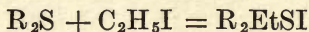
### THIOETHERS OR ALKYL SULPHIDES.

The thioethers are colourless liquids with a disagreeable odour, insoluble in water, but easily soluble in alcohol and ether. They are characterized by their additive powers; for example, they unite with alkyl iodides to form sulphine iodides.

One cc. ethyl iodide is added to 1 cc. of the thioether and the mixture warmed. After adding about a gram of moist silver oxide, the mixture is



shaken with water, again warmed and filtered. The filtrate will be strongly alkaline owing to the presence of trialkyl sulphoxide.



Methyl sulphide,  $(CH_3)_2S$ , B.P.  $37.5^\circ$ .

Ethyl sulphide,  $(C_2H_5)_2S$ , B.P.  $92^\circ$ .

*n*-Propyl Sulphide,  $(C_3H_7)_2S$ , B.P.  $130-135^\circ$ .

Allyl Sulphide,  $(CH_3 \cdot CH : CH)_2S$ , B.P.  $139-140^\circ$ , forms a crystalline precipitate with alcoholic mercuric chloride.

Thiophene,  $C_4H_4S$ , B.P.  $84^\circ$ .

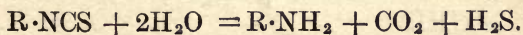
When a crystal of isatin is dissolved in 2 cc. conc. sulphuric acid, and to this solution a few drops of thiophene are added, a deep blue colour is produced.

## COMPOUNDS CONTAINING NITROGEN AND SULPHUR.

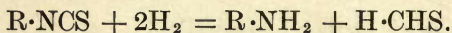
### MUSTARD OILS OR ISOTHIOCYANATES.

These are liquids with a very penetrating odour. They are insoluble in water. Their boiling points are lower than those of the corresponding thio-cyanates.

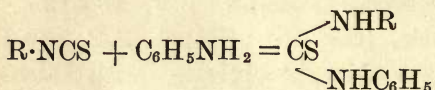
1. When heated to  $100^\circ$  with concentrated hydrochloric acid under a reflux condenser, they are decomposed into amines, sulphuretted hydrogen and carbon dioxide—



2. Reduction by means of zinc and hydrochloric acid produces an amine and thioformaldehyde, which has an odour of onions—



3. One cc. of the mustard oil is warmed with one cc. aniline for a few minutes. On cooling, a thiourea crystallizes out, and its melting point is determined (*see* p. 93).



4. If 1 cc. of the mustard oil be heated with one gram yellow mercuric oxide, an isocyanate and a black precipitate of mercuric sulphide are formed.

Methyl mustard oil,  $CSNCH_3$ , M.P.  $35^\circ$ .

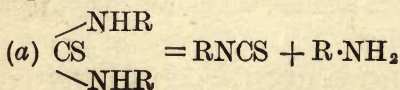
Ethyl mustard oil,  $CSNC_2H_5$ , B.P.  $131-132^\circ$ .

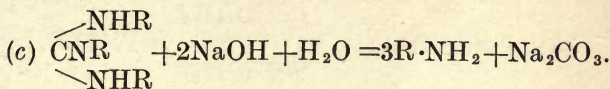
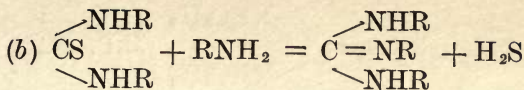
Allyl mustard oil,  $CSNC_3H_5$ , B.P.  $150.7^\circ$ .

Phenyl mustard oil,  $CSNC_6H_5$ , B.P.  $222^\circ$ , when reduced with zinc dust gives benzonitrile.

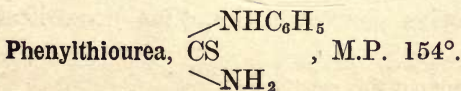
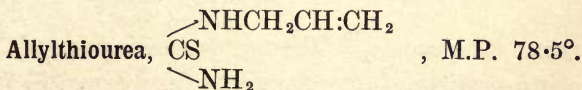
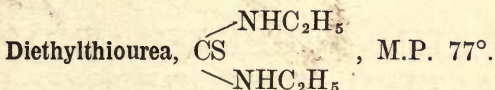
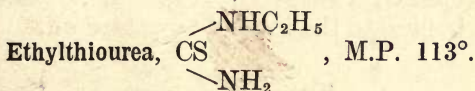
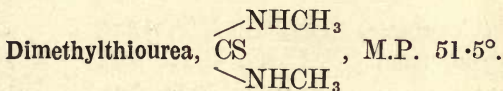
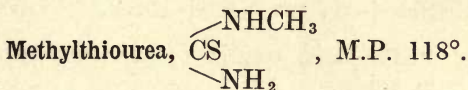
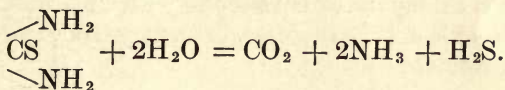
### THIOUREAS.

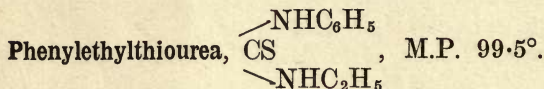
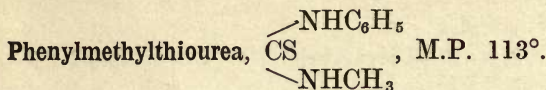
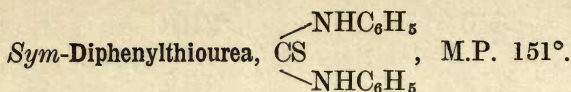
When a thiourea is heated with concentrated hydrochloric acid under a reflux condenser for some time and then distilled, the distillate contains a mustard oil. If the residue, which contains a guanidine derivative, be heated with concentrated caustic soda solution, an amine and a carbonate are produced.





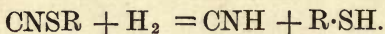
Thiourea,  $\begin{array}{c} \diagup \text{NH}_2 \\ \text{CS} \\ \diagdown \text{NH}_2 \end{array}$ , M.P.  $172^\circ$ , when boiled with alkalis, hydrochloric acid or sulphuric acid, is decomposed.





### THIOCYANATES.

1. When a thiocyanate is reduced with zinc dust and hydrochloric acid, a mercaptan and hydrocyanic acid<sup>1</sup> are produced—



2. Boiling nitric acid oxidizes thiocyanates to alkyl sulphonic acids.

Methyl thiocyanate,  $\text{CNSCH}_3$ , B.P. 133°.

Ethyl thiocyanate,  $\text{CNSC}_2\text{H}_5$ , B.P. 142°.

Allyl thiocyanate,  $\text{CNSC}_3\text{H}_5$ , B.P. 161°, rapidly changes on boiling to the isomeric mustard oil.

## XXXIII. TERPENES AND ALLIED COMPOUNDS.

THESE compounds, although possessing many of the properties of compounds already considered, have distinctive characteristics, thus necessitating

<sup>1</sup> Since hydrocyanic acid is a poison, great care must be taken in carrying out this reaction.



their separate classification. They are neither aliphatic nor aromatic, and are complex in structure. Nevertheless, they yield characteristic derivatives which as a general rule can be easily identified. They are all highly inflammable, possess characteristic odours and are insoluble in water, but are readily soluble in most organic solvents.

### HYDROCARBONS.

**Dipentene**,  $C_{10}H_{16}$ , B.P. 175–176°. The *dihydrochloride*,  $C_{10}H_{16} \cdot 2HCl$ , is prepared by passing dry hydrochloric acid over a few cc. dipentene for about one hour. The dihydrochloride separates on pouring the mixture on ice. It is dried on a porous plate and recrystallized from alcohol. M.P. 48–50°.

*Dipentene tetrabromide*,  $C_{10}H_{16}Br_4$ , can be made by adding bromine to a chloroform solution of dipentene, cooled to  $-10^\circ$  by salt and ice. The chloroform is removed by blowing a current of dry air through the solution. The tetrabromide on recrystallization from ethyl acetate, melts at 125°.

The active forms of dipentene are the **limonenes**. The active tetrabromides melt at 104°.

**Pinene**,  $C_{10}H_{16}$ , B.P. 155–156°.

The nitrosochloride,  $C_{10}H_{16}NOCl$ , melts at 115°. It is prepared by adding 1.5 cc. 33 per cent. hydrochloric acid to a mixture (cooled in ice) of 5 grams pinene, 5 grams glacial acetic acid, and 5 grams ethyl nitrite. After a short time the nitrosochloride

separates in large crystals. It is filtered off at the pump and washed with alcohol.

**Camphene**,  $C_{10}H_{16}$ , melts at  $51^{\circ}$ .

When heated with glacial acetic acid and a little sulphuric acid, camphene forms isobornyl acetate. On adding water the ester separates as an oil. It is hydrolysed with alcoholic caustic potash, the alcohol removed, and isoborneol is precipitated on addition of water. Isoborneol melts about  $208^{\circ}$  in a closed tube.

**Menthene**,  $C_{10}H_{18}$ , B.P.  $167-168^{\circ}$ . The nitroso-chloride melts at  $127^{\circ}$ .

### ALCOHOLS.

**Terpineol**,  $C_{10}H_{17}OH$ , melts at  $35^{\circ}$ . It forms a nitrosochloride melting at  $112-113^{\circ}$ .

**Borneol**,  $C_{10}H_{17}OH$ , M.P.  $203-204^{\circ}$ , and **Iso-borneol**,  $C_{10}H_{17}OH$ , M.P.  $208^{\circ}$ , yield derivatives of very similar melting and boiling points. The phenylurethanes of both melt at  $138-139^{\circ}$ .

**PREPARATION OF A PHENYLURETHANE.**—Molecular quantities of the alcohol and phenyl isocyanate<sup>1</sup> are mixed and heated rapidly to boiling. The mixture is well shaken and allowed to stand, the flask being closed with a calcium chloride tube. The unchanged phenyl isocyanate is extracted with benzene, and the residual urethane, after removal of benzene, is washed with cold water and recrystallized from ethyl acetate or a mixture of

<sup>1</sup> This preparation should be carried out in a draught-cupboard.

ether and petroleum ether. (Solvents containing "hydroxyl" should be avoided.)

When isoborneol is heated for some time with ethyl alcohol and concentrated sulphuric acid, isobornyl ethyl ether (B.P. 203–204°) is produced. Bornyl ethyl ether is not formed in this way.

Menthol,  $C_{10}H_{19}OH$ , M.P. 42°. The phenylurethane forms needles, melting at 111°.

### KETONES.

Carvone,  $C_{10}H_{14}O$ , B.P. 223–224°. On heating with a little acid it is converted into carvacrol.

Camphor,  $C_{10}H_{16}O$ , M.P. 177–178°. The oxime melts at 120°; the semicarbazone at 236°.

Menthone,  $C_{10}H_{18}O$ , B.P. 208°, has a peppermint-like odour. The semicarbazone melts at 184°.

## XXXIV. ALBUMINS AND PROTEIDS.

THESE are compounds of very complicated structure, and, with a few exceptions, do not crystallize. They are insoluble in the common organic solvents, but dissolve in aqueous solutions of acids and alkalies.

The following are general tests for the albumins :—

I. MILLON'S REAGENT (a solution of mercuric nitrate containing nitrous acid) gives an intense red colouration on heating.

II. XANTHO-PROTEIN REACTION. — By heating an albumin with fairly concentrated nitric acid, there separates a yellow flocculent precipitate of xanthoproteic acid, which dissolves in alkali giving an orange red solution.

III. BIURET REACTION.—When caustic potash is added to albumin, and then a very dilute solution of copper sulphate drop by drop, a fine violet-red colouration appears.

**Egg-albumin** is soluble in water and is precipitated from its solutions by metaphosphoric acid and by acetic acid. The precipitate is soluble in excess of the latter. Egg-albumin treated with concentrated sulphuric acid and sugar solution gives a red solution which changes to violet-red.

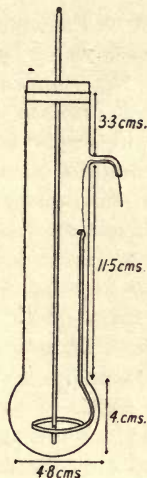
**Casein** contains phosphorus. An alkaline solution of casein dissolves cupric hydrate, giving a violet colour.

**Gelatine** contains sulphur. It is precipitated from its solutions by tannin.



## Appendix.

MELTING-POINT APPARATUS.—The sketch shows an apparatus which is very convenient and gives very



accurate determinations.

### SPECIAL REAGENTS.

NEUTRAL FERRIC CHLORIDE SOLUTION.—To some of the ferric chloride solution provided in the laboratory, dilute ammonium hydroxide or ammonium carbonate is added drop by drop until a precipitate just begins to form.

SCHIFF'S REAGENT.—Sulphurous acid is added to a dilute solution of rosaniline hydrochloride (magenta) until the colour just disappears.

**FEHLING'S SOLUTION.**—(1) 35 grams copper sulphate are dissolved in water and diluted to 1 litre. (2) 173 grams sodium potassium tartrate (Rochelle salt) and 70 grams caustic soda are dissolved in water and diluted to 1 litre.

These solutions are kept in separate bottles. Equal volumes of each are mixed immediately before making a test.

**SOLUTION OF IODINE IN POTASSIUM IODIDE.**—5 grams of iodine are dissolved in water containing 10 grams of potassium iodide and the solution made up to 1 litre.

**HYDRIODIC ACID.**—To obtain the constant boiling solution (Sp. Gr. 1.7) hydriodic acid of Sp. Gr. 2.00 is diluted with an equal volume of water and distilled over a small quantity of red phosphorus. The fraction boiling at  $125^{\circ}$ – $126^{\circ}$  is collected separately.

**SODIUM BISULPHITE (saturated solution).**—Sulphur dioxide is passed into a saturated solution of sodium carbonate for some time. Solid carbonate is added, from time to time, until no more dissolves. The final solution should smell strongly of sulphur dioxide.

**PHOSPHOMOLYBDIC ACID.**—To a solution of 75 grams ammonium molybdate in 500 cc. nitric acid (Sp. Gr. 1.2) and 500 cc. water, sodium phosphate solution is added until there is no further precipitate. This is then filtered off, well washed and finally warmed with sodium carbonate solution until completely dissolved. The solution is evaporated to dryness, and the residue ignited. The product is warmed with water and dissolved in a considerable excess of nitric acid.

**POTASSIUM MERCURIC IODIDE.**—13 grams mercuric chloride and 50 grams potassium iodide are dissolved in water and the mixture made up to 1 litre.

**MILLON'S REAGENT.**—A small quantity of mercury is dissolved in twice its weight of concentrated nitric acid in the cold and twice its volume of water is added.



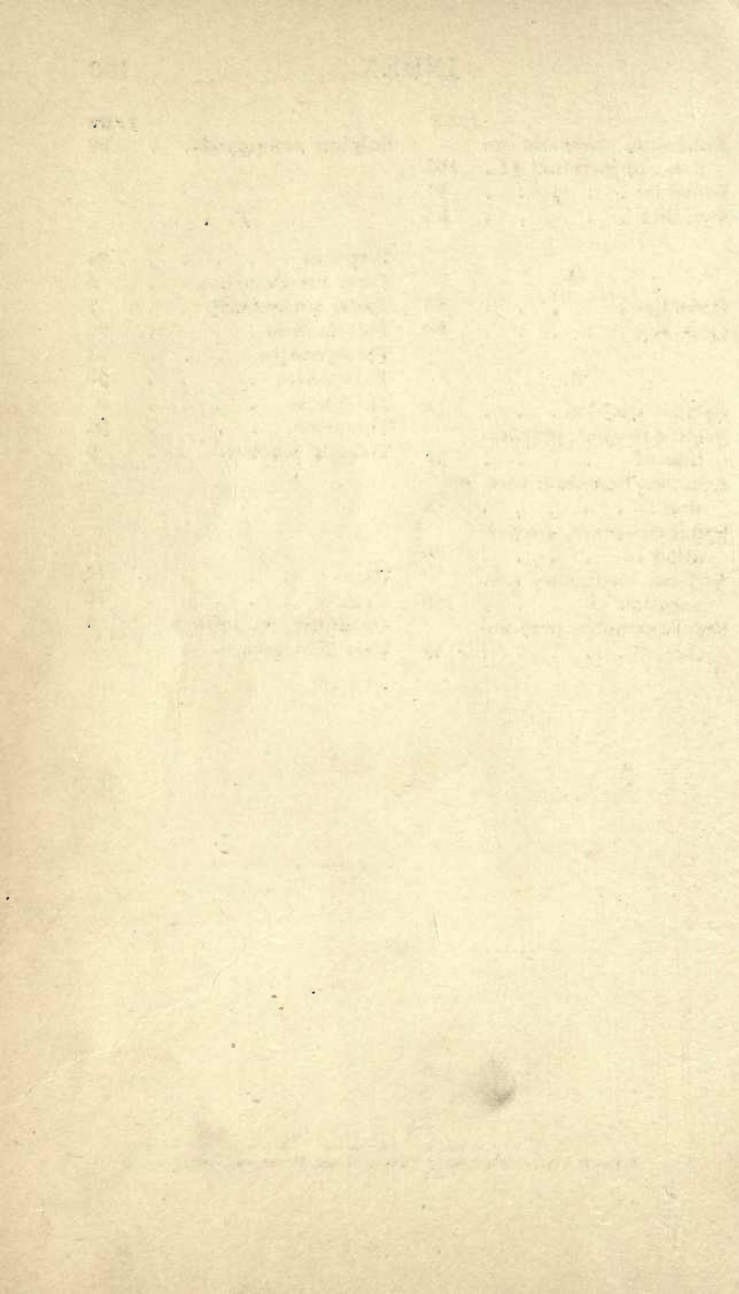
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$$(mNV)^{2/3}$$

$$(nML^3)^{2/3}$$

$$pv = MT$$

$$n^{2/3} M^{2/3} L^2$$

$$M^{2/3} L^2$$

















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